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### CHEMICAL CHARACTERIZATION OF THE PYROTECHNICALLY DISSEMINATED 66MM RED PHOSPHOROUS SMOKE SCREENING IR, VEHICLE LAUNCHED GRENADE

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## PREFACE

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Studies were conducted under and in compliance with current good laboratory practices (GLP). The performance of this study was consistent with the objectives and standards in "Good Laboratory Practices for Non-clinical Laboratory Studies" (21 CFR 58, Food and Drug Administration, U.S. Department of Health and Human Services, April 1988).

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# CHEMICAL CHARACTERIZATION OF THE PYROTECHNICALLY DISSEMINATED 66MM RED PHOSPHOROUS SMOKE SCREENING IR, VEHICLE LAUNCHED GRENADE

## 1. INTRODUCTION

Historically, the use of smokes and obscurants has been important to the military in various applications. Concealment, blinding, marking, signaling, and training are some examples of these applications.<sup>1</sup> The U.S. Marine Corps (USMC) and the U.S. Army currently use the M76 Smoke, Infrared Screening Grenade for protecting ground vehicles. The M76 family uses brass flakes, which have been shown to be an effective screening material in the visual through the thermal IR wavebands.<sup>2</sup> However, along with the poor yields associated with brass flakes, there is considerable safety, health, and environmental concerns from a manufacturing and an operational perspective.<sup>2-4</sup> The USMC has established the Red Phosphorous (RP) Grenade, 66mm Smoke Screening IR, Vehicle Launched MK1 MOD0 program to satisfy the need of redesigning the previously fielded M76 family of obscurants.<sup>2</sup> This program has developed a new design and payload that provides either equal or improved performance, while minimizing environmental and health impacts.<sup>2,3</sup>

Red phosphorous was chosen to replace the brass flakes as the payload for the 66mm Smoke Screening IR, Vehicle Launched Grenade. The RP has been widely used in screening applications where obscuration is achieved in various portions of the electromagnetic spectrum, including the visible range and in several IR bands. It has been deployed in either pots, grenades (66, 76, and 81mm), or 155 mm mortars.<sup>5</sup> The compound's chemical reactivity is considered intermediate to the stable black allotropic and the highly reactive white allotropic forms. The RP reacts slowly with oxygen and water vapor.<sup>5</sup> This, along with the fact that RP is the most common allotrope found in nature, made it a favorable choice for use in smoke payloads.<sup>5-9</sup> Generally, the production of smoke aerosol with an RP payload is accomplished through the combustion of P<sub>4</sub> (red allotrope) to form phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>), which chemisorbs with water to form phosphoric acid (H<sub>3</sub>PO<sub>4</sub>). Finally, condensation and hydration of phosphoric acid creates the aerosol smoke cloud.<sup>10</sup> As such, the smoke production is heavily dependent upon the amount of water in the air.<sup>10</sup>

Rheinmetall Weapons and Ammunition (RWM), Neuenburg, Germany, has been working for many years with RP in making improvements to this smoke technology. They have not only made improvements in the production of RP, but also the development of an innovative screening smoke grenade through the Rapid Reaction Multi-spectral Self Protection for Combat Vehicles or the MASKE system.<sup>10</sup> The smoke produced through the MASKE grenade is designed to provide visual and IR screening performance from observation and aiming devices, to counter threats from antitank guided weapons, and to prevent laser designation. The unique MASKE design is based on a “bi-modular concept,” which consists of a rapid reaction jamming module producing intense over-radiation based on thin RP flares, and a long-duration module producing visual and IR screening smoke based on RP pellets.<sup>10</sup> The RP payload consists of 130 g of the flares and 670 g of the pellet RP formulations. The RP flares are deflagrated upon bursting and cover the area spontaneously from the bursting point. The flare effect gives

immediate protection against observation, laser designation, and IR seekers by radiance in the IR range and smoke production in the visible range.<sup>10</sup> Upon ignition, the pellets are spread onto the ground in front of the point of burst. Smoke from the pellets closes the screen from the ground as they burn.<sup>10</sup>

The RP smokes have been evaluated in the literature;<sup>5,6</sup> however, data are required to ascertain the toxicity risk associated with the current formulation. For example, phosphine is a highly toxic material<sup>11</sup> that forms during long-term storage of RP smoke grenades, but has not been observed at high levels during standard disseminations.<sup>6,8</sup> Due to improvements in manufacturing the RP payload, it is expected that the production of phosphine will be less likely to occur.<sup>8,12</sup> However, each new formulation and/or hardware configuration must be examined to assure that risks and hazards associated with working with such smokes are not increased.<sup>7,9</sup> This study evaluated and characterized the combustion products observed after dissemination. This was accomplished by performing chemical and environmental characterization of the disseminated smoke.<sup>(7,9,13)</sup> Smoke aerosol and smoke residues were evaluated for aquatic toxicity using the fresh water daphnid, *Ceriodaphnia dubia* in a 7-day chronic toxicity assay and the marine fluorescent bacterium *Vibrio fischeri*, NRRL B-11177, in the Microtox assay. Therefore, suggestions and recommendations may be made after making comparisons to established threshold limits as set by regulatory agencies, such as the American Conference of Governmental Industrial Hygienists (ACGIH).<sup>14</sup>

Combustion product and chemical characterization testing for the 66mm RP Smoke Screening IR Vehicle Launched MK1 MOD0, which will be discussed further as the 66mm RP grenade, was accomplished in a dynamic system inside an enclosed shed. In this scenario, the highest concentration of combustion products would be attained inside the shed and would not represent real world scenario (i.e., open air dissemination) for this specific munition (66mm RP grenade).

## 2. MATERIALS AND METHODS

### 2.1 Materials

#### 2.1.1 66mm RP Grenades

One pallet (40 grenades) of 66mm RP grenades was transported to the U.S. Army Edgewood Chemical Biological Center (ECBC), Aberdeen Proving Ground (APG), MD, from the Naval Surface Warfare Center (NSWC), Dahlgren Division, VA, and stored at the ECBC Engineering Directorate's Ammunition Storage Facility. The smoke payload consisted of two layers. The first layer was the short burning flares, and the second, longer burning, layer consisted of RP pellets.<sup>15</sup> All grenades were kept in their respective ammunition cans during storage. On days of testing, one 66mm smoke grenade (Figure 1) was delivered from the storage facility to a downrange open field testing site for dissemination, sampling, and analysis. At the start of the long-term storage test (November 07), five ammunition cans (4 grenades each) were transported to the Engineering Directorate's climatically controlled chamber to monitor phosphine gas emissions.

Table 1. 66mm grenades tested at ECBC.

NSN	1330-01-559-7164
Lot Number	BCK07B001-1031
DOT Nomenclature	Ammunition, Smoke UN0016
US Interim Hazard Class	1.4G



Figure 1. 66mm RP smoke grenade, MK1 MOD0.

#### 2.1.2 Reagents and Standards

Potassium hydroxide and a stock standard consisting of five anions used for calibration were purchased from Dionex (Sunnyvale, CA) and  $\text{SO}_4^{2-}$ . The manufacturer's certificate of analysis confirmed the anions and their concentrations as  $\text{F}^-$  (20.1 mg/L),  $\text{Cl}^-$  (29.9 mg/L),  $\text{NO}_3^-$  (100 mg/L),  $\text{PO}_4^{3-}$  (152 mg/L), respectively.

The Mg (in 4% $\text{HNO}_3$ ) and P (in water) PlasmaCal standards were purchased from SCP Sciences (Champlain, NY). The corresponding certificate of analysis confirmed the standard as 1000  $\mu\text{g}/\text{mL}$  (ppm). A 1000-ppm (0.5 M  $\text{HNO}_3$ ) standard for K was purchased from Fluka (St Louis, MO).

A 0.5-ppm phosphine/nitrogen gas mixture (Lot No. 84271)(34 L) was obtained from AL Compressed Gases (Spokane, WA). A volume of 0.5-1.0 L was transferred from the can into an inert 1-L Tedlar (Du Pont, Remington, DE) sampling bag (SKC, Inc., Eighty Four, PA). Gas-tight syringes were inserted through the septum of the bag and used to draw differing volumes of the mixture for calibration standards.

Hydrochloric acid (HCl) and nitric acid ( $\text{HNO}_3$ ) were purchased from Fisher Scientific (Pittsburgh, PA).

The distilled water was generated from municipal water at ECBC. Municipal water was passed through a carbon filter, a water softener system, and a Hero 205 reverse osmosis (RO) system. Then the water was stored in a pressurized holding tank and sent through a Barnstead Nanopure System containing pretreatment, high capacity de-ionization, ultra pure mixed bed de-ionization, and organic removal cartridges. This water was then distilled using a Corning MP-6A glass still and stored in a glass holding tank until needed.

## 2.2 Experimental Design-Downrange Testing

All grenades were disseminated in accordance with (IAW) locally established standard operating procedures for the safe handling of ammunition and pyrotechnics. Disseminations were conducted on a large concrete pad routinely used for outdoor field tests. A wooden shed with an approximate volume of  $21.823 \text{ m}^3$  (Figure 2, left) was used to partially contain the smoke. The smoke aerosol was collected from within the shed (Figure 2, right). Each grenade consisted of two separate phases in one container. One phase is made up of RP flares; whereas, the second phase is made up of RP pellets. Both compositions are ignited and spread by the same bursting charge. Upon firing with an electric fuse, the ejection charge is ignited, a pyrotechnic delay-element is ignited, and after 1.2 s, the delay element ignites the bursting charge that opens the canister and ignites, which spreads the payload. A four-legged stainless steel stand was erected to hold the grenade (Figure 3, left). At the top and center of the stand, a band-clamp was placed to hold the grenade. To control the spreading of the flares and pellets, a 55-gal stainless steel drum was hoisted directly over the center of the stand holding the grenade (Figure 3, left and right). The drum was held over the center of the four-legged stand by nylon rope. Six shallow, stainless steel pans were placed directly below the 55-gal drum (Figure 3, right). The 55-gal drum was lowered over the grenade and stand such that about 2-3 in. of space was left between the legs of the stand and the bottom of the drum (Figure 3, right). Upon firing, the flares and pellets impacted the sides of the 55-gal drum, which forced the burning payload to fall onto the stainless steel pans (Figure 2, right). As the payload burned, the RP smoke was generated and filled the shed (Figure 4, top and bottom). The bursting charge ignition was the start of the dissemination.

Samples were collected inside the shed approximately 3 ft above the ground and at a distance of approximately 3.5 ft from the grenade. Figures 2 (right) and 5 (left and right) show the placement of the sample collection devices inside the wooden shed and their proximity to the grenade. Figure 6 shows the grenade at the conclusion of a field test following ignition and dissemination. As Figure 6 also shows, the grenade was completely blown apart, and the burnt residue of the payload was collected inside the pans as a black residue.



Figure 2. Wooden sheds used for smoke dissemination containment and sample collection (left), and with sample collection devices, jug, pumps, and tubing in place (right).



Figure 3. Grenade holding stand, drum, and sample pans used for smoke dissemination inside wooden shed. Left: four-legged stand with band-clamp and 55-gal placement and electric fuse wiring. Right: Placement of drum over the grenade for flare and pellet collection.

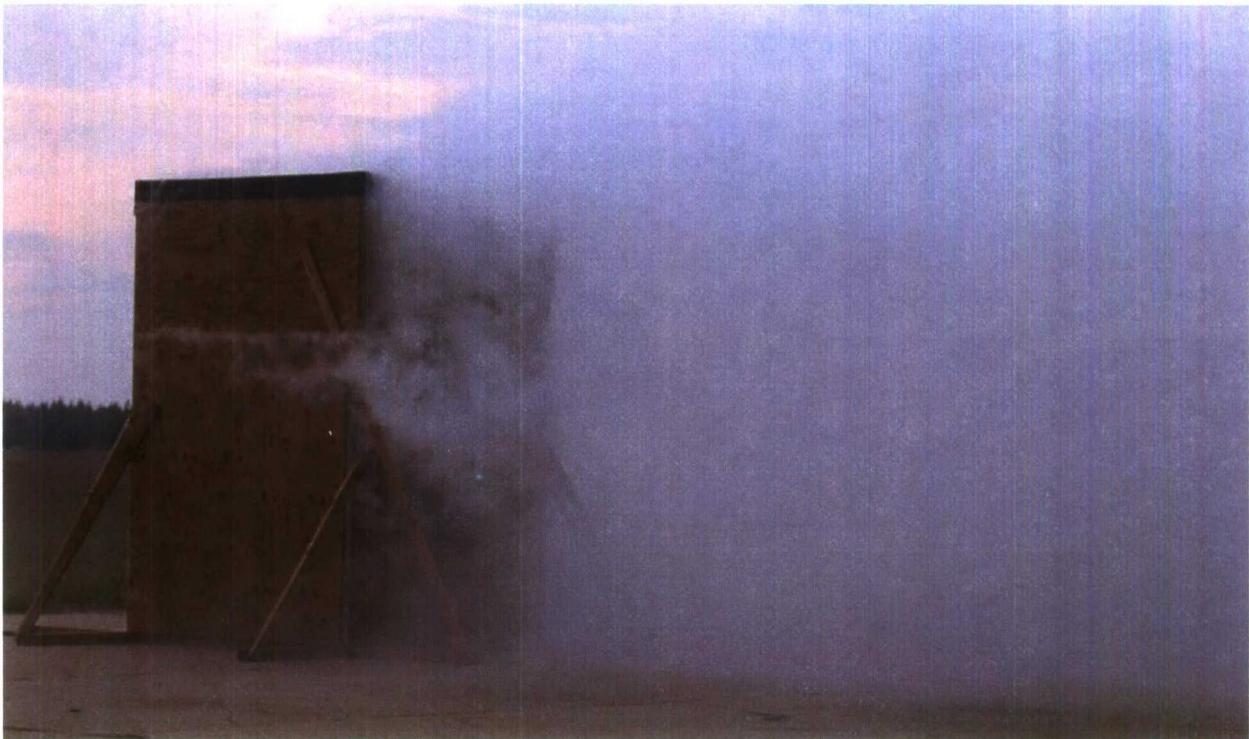


Figure 4. Smoke production from the dissemination of a 66mm RP grenade. Top and Bottom: Various time periods during smoke dissemination.



Figure 5. Sample collection placement and location within the collection shed. Left: Sampling equipment on shelf inside shed. Right: Placement of sample collection devices in relation to grenade and grenade holding and containment devices.

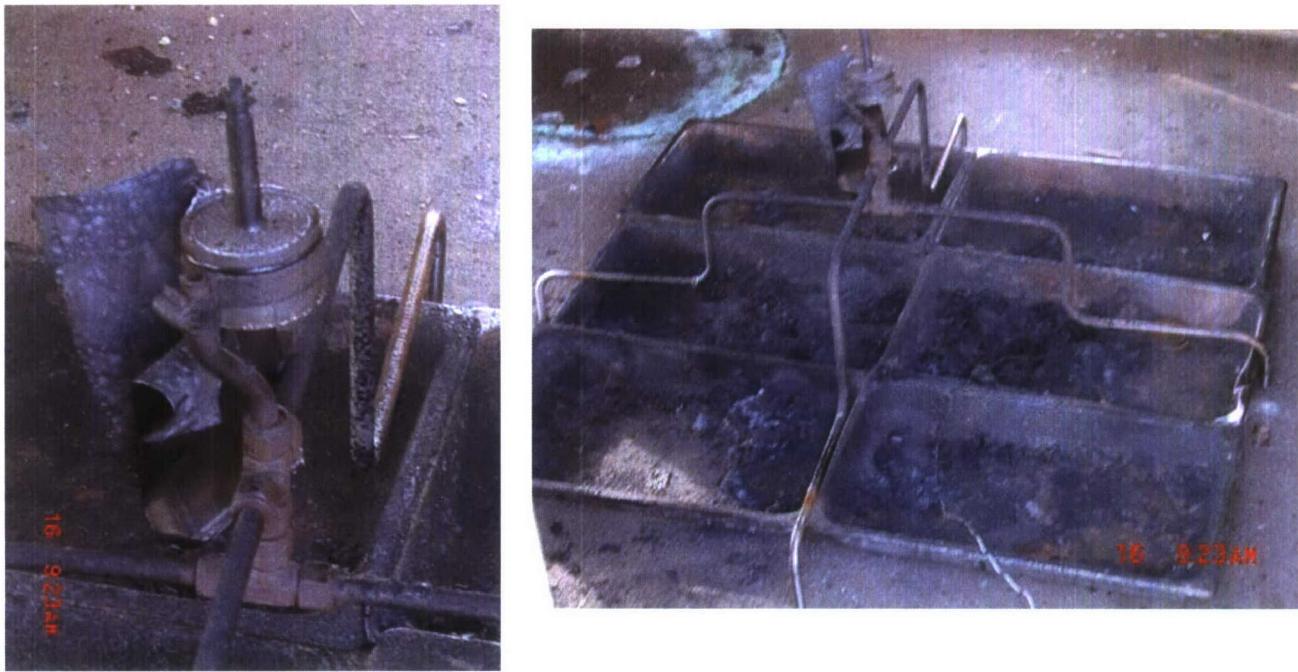


Figure 6. Pictures following smoke dissemination for 66mm RP grenade. Left: Close up of grenade bottom still in holder. Right: Carbonaceous material left behind following a typical dissemination.

## 2.3 Field Collection

### 2.3.1 Shed Concentration

Six 25-mm A/E Glass Fiber Filter (GFF) pads (Pall Corporation, Albany, NY) were used to collect the generated smoke particulates to determine the total aerosol concentration. The pads were weighed and placed inside the holders to allow attachment to vacuum pumps. Samples were drawn at an approximate flow rate of 1 L/min. Prior to each dissemination, the flow across each GFF pad was measured individually with a Bios International (Butler, NJ), Drycal, DC-Lite external flow measuring device. Samples were pulled for 30 s once the shed was visibly filled with smoke (within 1 min). Gravimetric analysis, using a Mettler Toledo MX5 microbalance (Mettler Toledo, Columbus, OH), was used to determine the mass collected on each of the pads. These same pads were also used to determine metals and anions in the particulate material collected. Calibration of the balance was performed with American Society for Testing and Materials (West Conshohocken, PA) Class 1 weights. Filter holder assemblies were sonicated and cleaned prior to the next use.

## 2.3.2 Particle Size Collection

### 2.3.2.1 Cascade Impactors

Cascade impactors (Sierra Instruments, Monterrey, CA) were used to monitor the particle size distribution of the generated smoke cloud. For each grenade, air was drawn from the shed through the impactor at approximately 7 L/min (as specified by the manufacturer) for 30 s. The GFF substrates were used to collect the particles on the individual stages. Two impactors were used for several disseminations. The first impactor measured particle size 1 min following start of smoke generation, and the second impactor measured 4 min following start of smoke generation. Gravimetric analysis using a Mettler Toledo MX5 microbalance was used to determine the mass collected on each stage of the two impactors.

### 2.3.2.2 Particle Size Determination by Aerodynamic Particle Sizer

An aerodynamic particle sizer (APS) spectrometer (model 3321, TSI, Inc., Shoreview, NM) was placed on an open concrete pad approximately 20 m down wind from the grenade's point of activation.. Two aerosol dilutors (model 3302A, TSI, Inc., Shoreview, NM) fitted with 1:20 capillaries, were stacked on top the APS. Flows were verified using a flow standard (model Gilian Gilibrator II Calibrator, Zefon International, Inc., Ocala, FL), and pressure drops were set for proper dilution. The APS was programmed to take numerous 10-s sequential samples and started prior to smoke dissemination. The data from the APS was then used to determine the mass median aerodynamic diameter of the smoke generated from the grenade as would be expected from a real world scenario.

## 2.3.3 Volatile Organic Combustion Products (VOCs)

Smoke vapor samples were drawn and collected onto 10-mm multibed sorbent tubes (CDS Dynatherm, Inc., Oxford, PA) (part #AO-06-2731) packed with equal portions of Tenax-TA, Carboxen 1000, and Carbosieve S111. Three sorbent materials were used to assure that high and low molecular weight compounds would be trapped during the dissemination. All sampling tubes were conditioned at 300 °C for 30 min with nitrogen flow at 50 mL/min. Atmospheric blanks inside the sampling shed were collected from the surrounding air before each dissemination. During the dissemination, two additional tubes were used to sample the smoke cloud for VOCs. To prevent aerosols from passing into the tubes, GFF pads were attached to the front portion of each tube. Flow rates were checked against a separate external flow-measuring device (Drycal, DC-Lite, Bios International, Butler, NJ). Flow rates were set at approximately 1 L/min for 3 min to assure that a sufficient quantity of air was drawn to detect lower concentrations of potentially toxic compounds.

Thermal Desorption Gas Chromatography Mass Spectrometry (GC/MS) was used to analyze for VOCs. Prior to injection onto the GC/MS, all field samples were concentrated within the thermal desorption system onto a trap CDS Dynatherm, Inc., (Oxford, PA) part #AC-06-5223) containing the same three sorbents that were used during field collection. The thermal desorption system was a CDS Analytical ACEM 900 system, and the GC/MS system was an Agilent 6890 GC equipped with a 5973 mass selective detector. Separation conditions were

IAW the approved National Institute for Occupational Safety and Health (NIOSH) Manual of Analytical Methods 2549.<sup>16</sup>

### 2.3.4 Inorganic Gas Collection

A 13-gal low-density polyethylene (LDPE) carboy was used as a vacuum reservoir (Figure 7) to collect inorganic gases. A hole was drilled into the lid of the carboy and fitted with a polyvinylchloride (PVC) schedule 40 fitting. This fitting was sealed with a butyl rubber gasket. A Tedlar bag (Du Pont, Remington, DE) was attached to the inner lid portion of the PVC fitting with a stainless steel band clamp and a pipe weld fitting to a 3/8-in. swagelok tube. A 47-mm filter housing was attached to the 3/8-in. swagelok tube protruding from the outer portion of the lid. When assembled, the bag had an opening through the lid and filter housing to the outer atmosphere. A ½-in. thread [National Pipe and Thread (NPT) was tapped into the top portion of the carboy, and a ½-in. male NPT ¼-in. swagelok fitting was threaded into this hole. One end of a ¼-in. LDPE line was attached to the ¼ in. swagelok fitting (via double end shut off quick connects), and the other end was attached to a vacuum pump. When the pump was started, a negative pressure was created in the carboy, thereby pulling atmospheric air through the filter into the bag. The length of sampling was approximately 1 min at the maximum flow of the pump. The volume of sample collected was not critical as the gas collection was meant to pull in as much vapor as possible.



Figure 7. Experimental design for trapping inorganic gases.

Gas samples were pulled from the carboy into a 1-L Tedlar bag using a 1-L Hamilton Syringe (Hamilton Co., Reno, NV). The gas was pulled onto compound specific detector tubes (Kitagawa, Schaunberg, IL) using a Matheson (Newark, CA) portable gas sampling pump (Model 400). Concentrations were recorded by monitoring the colorimetric change observed on the sorbent material. Phosphine ( $\text{PH}_3$ ), hydrogen chloride ( $\text{HCl}$ ), hydrogen cyanide ( $\text{HCN}$ ), hydrogen fluoride ( $\text{HF}$ ), carbon monoxide ( $\text{CO}$ ), carbon dioxide ( $\text{CO}_2$ ), formaldehyde ( $\text{HCOH}$ ), nitrogen oxides ( $\text{NO}_x$ ), ammonia ( $\text{NH}_3$ ), and sulfur dioxide ( $\text{SO}_2$ ) were

all monitored after each dissemination. Table 2 lists the Manufacturer's (Kitagawa) tube part numbers along with their respective measuring range.

Table 2. Kitagawa part numbers and measuring ranges for tested inorganic gases.

Inorganic Gas	Manufacturer Part No.	Measurable Range (ppm)
NO <sub>x</sub>	8014-175U	0.5-30
PH <sub>3</sub>	8014-121SC	0.05-2
	8014-121U	20-1400
HF	8014-156S	0.17-30
NH <sub>3</sub>	8014-105SC	5-260
CO	8014-106S	10-250
HCN	8014-112SB	0.5-100
HCHO	8014-171SB	1-35
SO <sub>2</sub>	8014-103SE	0.25-10
HCl	8014-173SB	0.4-40
CO <sub>2</sub>	8014-126SF	100-4000

### 2.3.5

#### Inorganic Anions: Ion Chromatography and Sample Prep

Six 25-mm A/E GFF pads were used to collect aerosol samples for concentration determination during the smoke dissemination as given in Section 2.3.1. Following gravimetric analysis, the pads were placed in 50-mL conical polypropylene (PP) vials with caps for subsequent sample preparation and analysis. Three of the GFF pads were subsequently prepared for determination of anions. Five milliliters of water were added to each of the three 50-mL conical vials containing the GFF pads and sample. The vials were shaken for 10 s and allowed to sit for 30 min. One additional blank GFF pad was subjected to the same sample preparation conditions and used as the control. The solution was transferred to 5-mL conical vials and filtered using 13-mm nylon syringe filters (Millipore Corp., Bedford, MA). Dilutions were made as necessary to bring the sample concentrations into the calibration range. A 1:1000 dilution of the samples was made for all phosphate determinations.

Ion chromatography was used for the analysis of anions collected on the GFF pads. The instrumentation was an ICS-2000 Series Dionex Ion Chromatograph with conductivity detection (IC-CD). A Dionex anion exchange column (IonPac AS18 4 x 250 mm, analytical) and guard column (IonPac AG18 4 x 50 mm) were used. The isocratic separation was accomplished using a 30-mM potassium hydroxide (KOH) EluGen Cartridge (EGC II) mobile phase with a flow rate of 1.0 mL/min. Injections were made using an AS40 Automated Injector (Dionex) (25 µL). Detection was accomplished using an anion self suppression system with conductivity detection. Analytical methodology was IAW the NIOSH approved method #7903 with modifications appropriate for instrument and method modifications and upgrades.<sup>17</sup>

## 2.3.6

### Metal Analysis

#### Metal Analysis-Acid Digestion, Percent Recoveries, Smoke Analysis

The metals used in pyrotechnics are generally found to be in an oxidized form following combustion. This often leaves the metal oxide insoluble and requires it be reduced to an elemental form before analysis by inductively coupled plasma-optical emission spectroscopy (ICP-OES). This is accomplished through acid digestion, which applies concentrated acids and heat to break the oxide bonds. An acid digestion method for P, Mg, K, and the following oxides: PO<sub>4</sub>, P<sub>2</sub>O<sub>5</sub>, KOH, or K<sub>2</sub>O, and MgO was developed.

The acid digestion was accomplished using a *Digi-Prep Hot Block Apparatus* (SCP Sciences, Champlain, NY). The hot block conditions were the same for all metals analyzed. Two and one half milliliters of hydrochloric acid (HCl) was added to each 50-mL PP vial with pre-weighed metal and/or metal oxide and one 25-mm GFF pad. The hot block was brought up to 95 °C over a 45-min period and held at 95 °C for 15 min. The vials were removed from the hot block and allowed to cool for 5 min. Following cooling, 2.5 mL of concentrated nitric acid HNO<sub>3</sub> was added to the vials, and placed into the hot block. The hot block was brought back up to 95 °C over a 35-min period and held at 95 °C for another 15 min. Vials were removed from the hot block and allowed to cool. The solution was transferred to a 50-mL PP volumetric flask (VF). Each vial was rinsed three to five times with deionized water and transferred to the VF, which was then brought up to volume. No dilutions were necessary.

Metal oxide standards were used to determine the percent recoveries of the acid digestion methodologies for each metal with >80% extraction efficiency. NIOSH Method 7303 was used to determine parameters for acid digestion and detection methods.<sup>18</sup> Percent recoveries were determined for the principal metals contained in the 66mm RP grenade payload through quantitative analysis using a Perkin Elmer Optima 5300 DV Series ICP-OES (Boston, MA) equipped with OES for elemental detection and quantification. The wavelengths (nm) used were 280.271 and 279.553 for Mg, 213.617 and 214.914 for P, and 766.490 for K. Methodology guidance was IAW ICP-OES software and hardware documentation.

The ICP-OES was used to analyze the material collected on the GFF pads during the disseminations. As previously stated in Section 2.3.5, six 25-mm A/E GFF pads were used to collect aerosol samples during the smoke dissemination. Following gravimetric analysis, three of the GFF pads were subsequently prepared for metal analysis following the acid digestion procedure given above.

Weighed aliquots of solid metal oxides of MgO (99.999%), KOH (>85%), [purchased from Sigma-Aldrich (St. Louis, MO), KNO<sub>3</sub> (Fluka, St. Louis, MO), K<sub>2</sub>SO<sub>4</sub> (99% anhydrous), and Na<sub>2</sub>HPO<sub>4</sub> (Anhydrous) (Fisher Scientific, Pittsburgh, PA), were placed into 50-mL conical PP vials (SCP Sciences, Chamberlain, NY).

## 2.4 Long-Term Storage Test

### 2.4.1 Long-Term Storage Test - Experimental Design

Five ammunition cans were placed inside a 5 ft x 5 ft x 5 ft (125 ft<sup>3</sup>, 3.54 m<sup>3</sup>) static, climatically controlled aging chamber (Figure 8). Three cans were placed onto a metal shelf inside the chamber (Figure 8, top). Two cans were placed on the bottom grating of the chamber and were fitted for air sample collection to investigate possible PH<sub>3</sub> off gassing throughout the long-term storage test (Figure 8, top). Prior to placing the two cans into the chamber, the grenades were removed, and sample lines were put into the ammunition cans for sample collection. Two 9/16-in. holes were drilled into the sides of each ammunition can on the side near the latched end. One hole was drilled toward the top (vent line) and the other toward the bottom (sample line). A stainless steel 1/16-in. male connector, O-seal to straight thread [Baltimore Valve and Fitting (Baltimore, MD)] part #SS-100-1-OR was inserted into the holes, from the outside, and secured with a 5/16 in.-24 stainless steel nut (McMaster-Carr, Elmhurst, IL) part #94804A315. To each of the holes, one end of a 4 ft, 1/16-in. o.d./0.03-in. i.d. TFE tube (Alltech, Deerfield, IL part #35670) was connected to the male connector via the compression fitting (Figure 8, middle). To the other end of the tubing, a 1/16-in. stainless steel union (Baltimore Valve and Fitting part #3 SS-1F0-6GC) was connected via the compression fitting. A piece of stainless steel tubing 1/16-in. o.d./0.04-in. i.d. (Popper and Sons, New Hyde Park, NY, part #9563) was used as an insert on the other end of the union to form a seal. Luer adapters, a male (Popper and Sons part #6523) in the case of the vent line and a female for the sample line, (Popper and Sons part #6528) were attached to the union. Male- and female-closed end luer lock plugs (Popper and Sons parts #6517 and #6200, respectively) were used to close the lines when not in use. Once the ammunition cans were retrofitted with the sample and vent lines, the grenades (four each can) were placed inside the ammunition cans. The ammunition cans had approximately 3 L of dead volume when grenades were inside.

Sample and vent lines were run through the holes in the chamber to the outside room (Figure 8, bottom). The long-term storage timeline was calculated using the Arrhenius Relationship for accelerated testing.<sup>(7,19)</sup> The temperature was set at 158 °F (70 °C) held at 30% relative humidity (%RH). At this temperature, the natural aging from 1 year may be simulated in 2.298 weeks.<sup>19</sup> Therefore, to simulate 5 years, 11.49 weeks at 158 °F was required. The start date was 6 November 2007 at 1300 hr, and the end date was 29 January 2007 at 1300 hr. Blank samples of the air space in the chamber and inside the ammunition cans were drawn prior to experiment start.

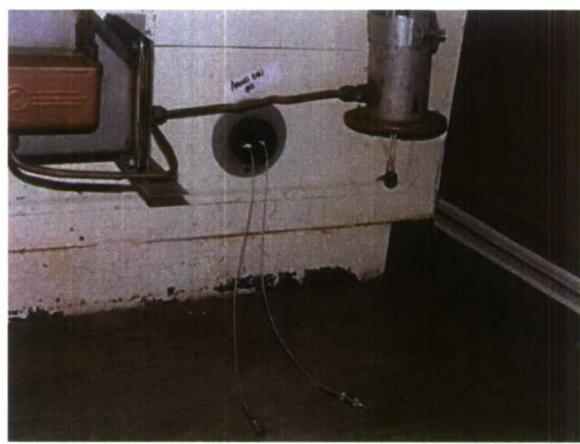
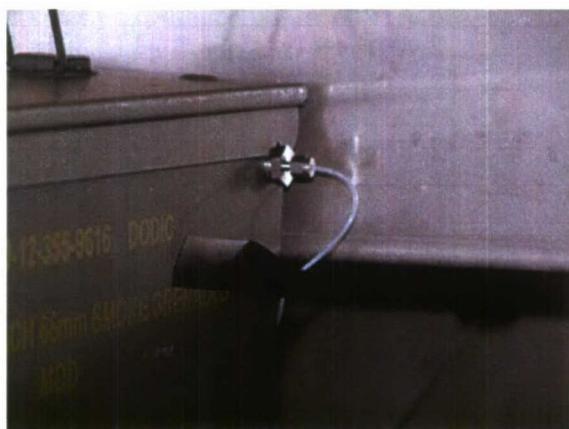


Figure 8. Ammunition cans (with grenades inside) placed inside the climatically controlled chamber [5 ft x 5 ft x 5 ft (top)]. Placement of the sampling tubes on the ammunition cans (middle) and placement of the sampling tubes outside the chamber (bottom).

## **2.4.2        Long-Term Storage Test - Gas Sampling**

Gas samples were pulled from the dead space inside each of the ammunition cans once per week to monitor for the possible production of PH<sub>3</sub> gas. Gas from inside each of the ammunition cans and the chamber was pulled through the sampling tube with a 1-L Hamilton Syringe (Hamilton Co., Reno, NV). Two hundred milliliters were slowly pulled to prevent possible water condensation and allow for temperature equilibration) from each ammunition can. A 1-L sample was also pulled from inside the climatically controlled chamber. After pulling the sample, the small fitting on the front of the 1-L syringe was closed, and the syringe was allowed to cool for approximately 20-30 s. A latex tube was placed on the valve and connected to a 1-L Tedlar bag (A-L Compressed Gas, Spokane, WA) (Du Pont, Remington, DE) at which time the sample was dispensed. Between each sampling, the Hamilton Syringe was purged with 5 L of air to eliminate cross contamination.

At the conclusion of the long-term storage test, the three ammunition cans that were untouched throughout the experiment were sampled. The dead space gas inside each can was sampled to determine the overall concentration of PH<sub>3</sub> that off gassed over the 5-year simulated test period (12 weeks). Holes were drilled into the sides of the ammunition can to sample the air. One hole was drilled into the upper back portion of the can, and a rubber stopper was used to immediately seal the hole. A hose barb fitting was attached to a syringe (Hamilton Syringe) via a rubber tube and stopcock. A second hole was drilled into the lower front portion of the can, and the hose barb fitting was immediately sealed to the hole with duct seal. The stopcock was opened, the rubber stopper from the back of the ammunition can was removed, and air from inside the can was removed by syringe. The stopcock was then closed, and the hose barb was removed. Sample volumes of 360 - 400 mL were transferred to 1-L Tedlar bags.

## **2.4.3        Long-Term Storage Test - Analytical Methods**

### **2.4.3.1      Phosphine Detector Tubes**

Gas samples were pulled from the Tedlar sample bags onto a PH<sub>3</sub>-specific detector tube (Kitagawa, Schaunberg, IL), IAW air volumes determined by the manufacturer, using a Matheson portable gas sampling pump (Model 8410). Concentrations were recorded by monitoring the colorimetric change observed on the sorbent material.

### **2.4.3.2      Phosphine GC-FID Method**

Thermal desorption GC-Flame Ionization Detection (FID) from Agilent (Palo Alto, CA) with a Dynatherm (ACEM-900, CDS Dynatherm, Inc., Oxford, PA) sample introduction system was used to analyze PH<sub>3</sub>. A 60-mL sample of air was pulled through a three-bed sorbent tube (Dynatherm), containing Tenax TA, carboxen, and carbosieve sorbent materials using a 60-mL gas tight syringe. Samples were introduced using a Dynatherm sample introduction system, which effectively desorbed the PH<sub>3</sub> from the sorbent material onto the GC column. The column used for the separation of the PH<sub>3</sub> was a Vocol 60 m x 250 µm i.d. (1.5-µm thickness) (Supelco, Bellafonte, PA). The initial oven temperature was held at 30 °C for 1 min and programmed to increase to 225 °C at 5 °C/min. This temperature was maintained for 11 min. A column flow of 5 mL/min nitrogen was used as the carrier gas. Phosphine was detected by FID.

A 0.5-ppm PH<sub>3</sub> standard (N<sub>2</sub>, 34 L, A-L Compressed Gas, Portland, OR) was used to develop the GC-FID method and to calibrate the instrument. Several different volumes of the 0.5-ppm PH<sub>3</sub> standard were applied onto the three-bed sorbent tubes for calibration.

#### 2.4.4 Long-Term Storage Test - Grenade Functionality

Following long-term storage testing, the grenades were taken downrange and fired to make sure that the grenades still functioned properly. Four of the five ammunition cans containing 16 grenades that had been subjected to the static temperature and RH conditions were taken down range, fired individually, and video recorded.

#### 2.5 Aquatic Toxicity Testing

##### 2.5.1 Smoke Sample Collection

Smoke aerosol (airborne smoke) was collected onto pre-weighed 45-mm glass fiber filters having a pore size of .45 µm via a vacuum line. Air was pulled through the filter at maximum flow of the pump for 60 s. The weight of the filters was determined, and the filters were placed in petri dishes and stored in a dedicator until needed for aquatic toxicity testing.

Smoke residue (fall out material) was collected from three separate grenade disseminations by placing six stainless steel trays below the grenade. Following the grenade burst, the burning RP pellet material was captured in the pans. Cool residue was placed into a 1-gal glass sample bottle.

##### 2.5.2 Sample (Extract) Preparation

Five filter pads were placed separately into 100 mL of media and gently swirled to extract the sample. The pads were removed from the media after 19 hr, and dried in a chemical hood for 19 hr at ambient temperature (22 °C) before being re-weighed. The difference between the filter pad weights before and after extraction was considered the nominal concentration in solution. The individual 100-mL extracts were combined into one bulk sample. The resulting nominal extract concentration was 3,313.3 mg/L with a pH of 2.5.

The bottle containing the smoke residue sample was mixed three dimensionally for 1 hr to ensure that the three grenade residue samples were mixed into one representative sample. A residue sample of 6,000 mg was placed into a 1-gal sample bottle and filled to 2 L with media. The sample bottle was placed on a shaker table at 30 rpm for 1 hr. The sample bottle was then allowed to sit over night (19 hr) to settle the residue particulates in the solution. The sample was poured through a Whatman ashless 41 filter (20-25 µm) to remove the large residue particulate. The resulting nominal residue concentration was 3,000 mg/L with a pH of 6.8.

The dissolved components of the extracts were not identified, and concentrations were not determined. Therefore, the concentrations reported here are to be considered nominal.

### 2.5.3 Microtox (MTX) Assay

The MTX assay\* exposes bioluminescent marine bacteria (*Vibrio fischeri*, NRRL B-11177), to a sample of unknown toxicity, so that changes in the output of bioluminescent light by the bacteria may be measured as a means of determining the level of toxic effects on the bacterial organisms. Under proper test conditions, the reduction in light output is a direct indication of metabolic inhibition. The bacteria were cultured by Azur Environmental (Carlsbad, CA)\* and shipped in lyophilized form. The bacteria (stored frozen) were re-hydrated immediately before testing. Individual assays were performed in a temperature-controlled photometer using glass cuvettes containing 1 mL of sample. For optimum accuracy in predicting toxicity, the bioassay must have a minimum of four dilutions exhibiting a dose response. At 5 and 15 min, the control and treatment groups were measured for light output. Data were analyzed using the MTX 100% test protocol software to determine the EC<sub>50</sub>, the effective concentration causing a 50% reduction in light output.

The initial salinity of the extracts was 0.2 and 0.3% for the residue and aerosol extracts, respectively. The optimal salinity for *Vibrio fischeri* is 2%. The salinities of the aerosol and residue extracts were adjusted to 2% by adding sodium chloride directly to the sample. Testing was also conducted using aerosol extracts that were pH adjusted to 6.1. The initial pH of the residue extract was 6.8, and pH adjustment was not needed. The extracts were diluted with media to produce nominal concentrations of 187.5, 375, 750, 1,500, and 3,000 mg/L for the residue extract, 3.2, 6.5, 13.0, 25.9, and 51.8 mg/L for aerosol extract, and 103.5, 207.0, 414.2, 828.3, 1,656.7, and 3,313.3 mg/L for pH-adjusted aerosol extract.

Quality control (QC) testing was conducted using ZnSO<sub>4</sub> x 7H<sub>2</sub>O as a standard toxicant. Using a standard whose toxicity is well known confirms the health of the test organism, and also checks the performance of the entire MTX system. The acceptable toxicity range for the 5-min EC<sub>50</sub> value is between 3 and 10 ppm (mg/L) for the ZnSO<sub>4</sub> x 7H<sub>2</sub>O standard, as prescribed by Azur Environmental.\* If the test result for the 5-min EC<sub>50</sub> value of the ZnSO<sub>4</sub> x 7H<sub>2</sub>O standard was outside this range, a new ZnSO<sub>4</sub> x 7H<sub>2</sub>O standard was prepared and tested. If the standard result was still out of the range, a new batch of bacteria from the same culture-lot was prepared, and the ZnSO<sub>4</sub> x 7H<sub>2</sub>O standard repeated.

### 2.5.4 Ceriodaphnia Assay (*Ceriodaphnia dubia*)

Ceriodaphnia Survival and Reproduction Assays were conducted according to the US Environmental Protection Agency standard methods.<sup>20</sup> The media for ceriodaphnia cultures consisted of 20% Perrier water and 80% RO water. Ceriodaphnia were fed a mixture of *S. capricornutum* (6 x 10<sup>5</sup> cells/mL) and cerophyl extract (10 µL/mL). The test chambers consisted

\*The AZUR Environmental product line is now owned and offered by Strategic Diagnostics, Inc.: Newark, DE.

of 30-mL plastic beakers containing 15 mL of solution. Ten replicates of controls and each treatment group were prepared, with each replicate containing one ceriodaphnia. The test media was renewed, and fresh food was added daily, for 7 days. Mortality and reproduction were recorded daily. A diurnal light cycle was maintained at 16 hr light and 8 hr dark. The light intensity was approximately 90 ft-c as measured at the top of the test chambers. The temperature was maintained at 25 °C. Ceriodaphnia were exposed to extracted smoke residue that was serially diluted with test media to obtain the nominal treatment concentrations of 12.5, 25, 50, 100, 200, and 400 mg/L for aerosol extracts and 62.5, 125, 250, 500, 1000, and 1500 mg/L for residue extracts. Testing was not conducted on pH adjusted aerosol extracts because pH of the buffered smoke aerosol was not a factor.

The QC testing was conducted by monitoring the reproduction of the control groups before initiating the definitive smoke extract tests. Offspring productivity in adults is a direct indication of the health of the population. At least 80% of the control organisms must survive, and 60% of the surviving adults must have had at least three broods with a total average of at least 15 offspring per surviving adult to meet acceptance criteria.

#### 2.5.5 Statistical Evaluation

Point estimation of EC<sub>50</sub> (the effective concentration that immobilizes 50% of the organisms) calculations were performed using the Probit Analysis contained in the Minitab™ (Minitab, Inc., State College, PA) statistical software package. The IC<sub>p</sub> (the concentration that causes inhibition of offspring production) was calculated using a linear interpolation method for calculating inhibition concentrations.<sup>21</sup>

Survival and reproduction data were subjected to hypothesis testing to determine the No Observable Effects Concentration (NOEC) and the Lowest Observable Effects Concentration (LOEC). Survival data were subjected to Fisher's Exact test to determine if there were any significant survival differences at the 95% confidence level between control and treatment groups. Reproduction data were subjected to One Way Analysis of Variance (ANOVA) to determine significant differences at the 95% confidence level among control and treatment groups. The Bonferroni's Multiple Comparisons test was used to determine which treatment groups were statistically different from the control. Treatment groups having no survival in any replicates were excluded from the NOEC and LOEC reproduction calculations. However, the treatment groups having no survival were included in the calculation of the EC<sub>50</sub> (effective concentration that produces a 50% adverse response) and IC<sub>p</sub> (inhibitory concentration that causes a percent reduction in offspring) endpoints.

### 3. RESULTS

#### 3.1 Shed Concentration

Because it is a dynamic system, the total concentration measured within the shed varied among disseminations. For these experiments, seven grenades were used to determine the chemical characteristics. For each dissemination, the temperature (T), wind speed (WS), dew

point (DP), RH, and atmospheric pressure (P) were measured and listed in Table 3. Over the duration of the study, the mean total particulate concentration in the shed was 68,132.19 mg/m<sup>3</sup> with a standard deviation (SD) of 11,497 mg/m<sup>3</sup> (n = 41). Table 4 gives the aerosol concentrations in milligrams per cubic meter (n = 6 for each dissemination) as well as the temperature (T, F) and the %RH for each dissemination.

Table 3. Meteorological conditions for disseminations by date.

	T*	WS <sup>#</sup>	DP <sup>^</sup>	%RH	\$P
10/11/2007	56.80	10.80	47.30	70.00	29.63
10/16/2007	59.60	7.36	55.90	87.50	30.16
10/18/2007	63.08	3.77	63.08	100.00	29.98
10/23/2007	69.30	8.38	64.72	85.33	29.94
10/30/2007	42.71	1.26	39.36	88.96	30.44
11/1/2007	57.75	7.18	53.88	86.88	30.04
11/6/2006	47.23	8.87	36.57	66.45	29.83

\*Temperature (°F)

<sup>#</sup>Wind Speed (mph)

<sup>^</sup>Dew Point (°F)

<sup>\$</sup>P Pressure (in. Hg)

Table 4. Average aerosol concentrations (mg/m<sup>3</sup>) determined for all disseminations with %RH and temperature (F).

Dissemination	(mg/m <sup>3</sup> )	SD <sup>^</sup>	T (F)	%RH
10/11/2007	54965.1 <sup>^</sup>	1906	56.80	70.00
10/16/2007	84993.4	2019	59.60	87.50
10/18/2007	78286.4	2892	63.08	100.00
10/23/2007	70151.0	3347	69.30	85.33
10/30/2007	58324.7	1425	42.71	88.96
11/1/2007	73303.6	4411	57.75	86.88
11/6/2007	54706.6	1557	47.23	66.45

<sup>^</sup>n = 5

### 3.2 Particle Size

#### 3.2.1 Particle Size from Inside Shed

Cascade impactors were used to measure the smoke aerosol size in the contained environment of the sampling shed. Samples were pulled for 30 s at 7 L/min (per manufacturer's specifications) at time points 60- and 240-s post start of smoke cloud dissemination. It was consistently observed that the particle size increased from the 60-s to the 240-s sampling (Table 5). At 60-s post start of dissemination, the particle size inside the shed ranged from 2.8 to 3.8 µm, and at 240-s post dissemination, the particle size was 4.3 to 4.8 µm. The measured particle sizes were unrealistic for an RP smoke device. This was attributed to either the high concentration leading to agglomeration or the hydrophilicity of the aerosol. To test this

hypothesis, the aerosol particle size was measured during an open-air dissemination with an aerodynamic particle size. Conducting the measurement in this way gave a more realistic particle size for the proposed usage of the device.

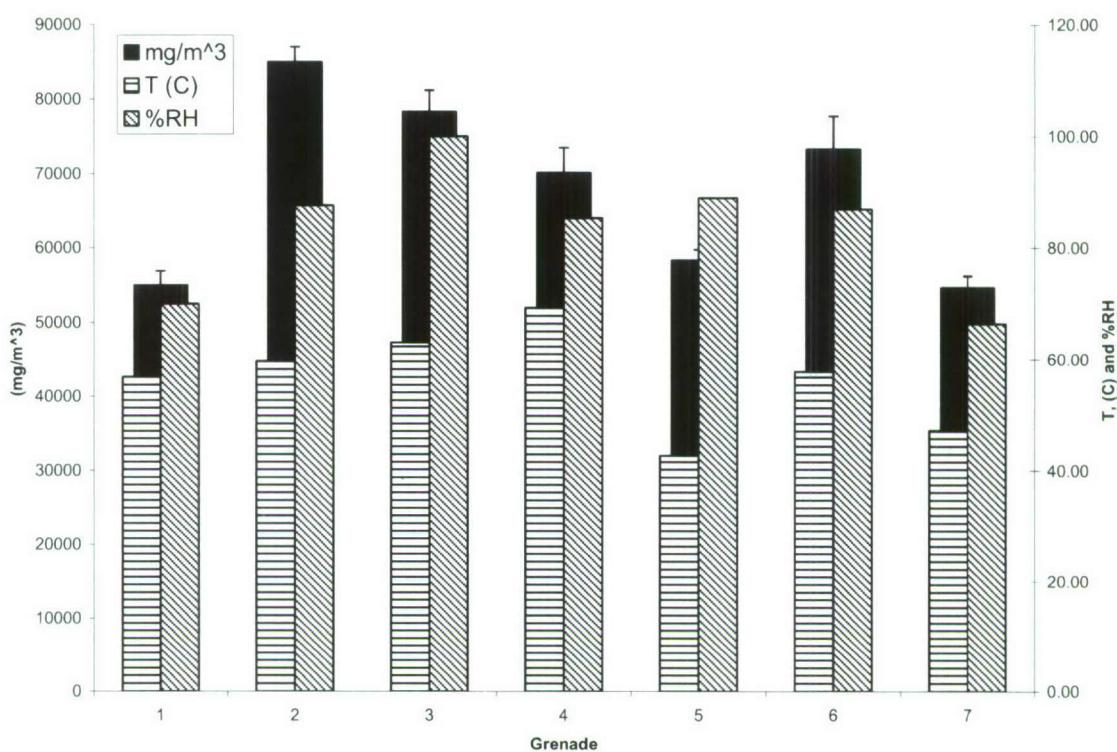


Figure 9. Bar graph depicting shed concentration (given on left axis) as well as %RH and temperature (F) (given on right axis).

Table 5. Particle size analysis from each 66mm RP grenade dissemination.

Date of Dissemination	Sample Time T+ (s)	MMAD ( $\mu\text{m}$ )	Geometric SD	Respirable Mass (%)
10/11/2007	60-90	3.14	1.87	58.390
10/11/2007	120-150	3.42	1.80	54.350
10/16/2007	60-90	3.63	2.00	51.921
10/16/2007	240-270	4.34	1.90	43.367
10/18/2007	60-90	3.79	2.00	51.650
10/18/2007	240-270	4.77	1.87	41.523
10/23/2007	60-90	2.81	2.38	57.087
10/30/2007	258-288	4.21	2.01	42.797
11/1/2007	60-90	3.67	1.97	51.081
11/6/2007	60-90	3.65	1.98	53.776
Average		3.743	1.978	50.594
Stdev		0.58	0.16	6.01
%RSD		15.42	7.99	11.89

### 3.2.2

#### Particle Size of Disseminated Smoke Down Wind of Initiated Grenade.

From these experiments, the particle size of the disseminated smoke was  $1.032 \pm 0.06$  with a  $\sigma_g$  of  $1.332 \pm 0.03$  ( $n = 6$ ). These measurements were taken within the obscurant cloud (down wind of grenade activation) over a 60-s period (10 s/sample) following grenade firing).

### 3.3

#### VOCs

Figure 10 depicts a sample chromatogram obtained after analyzing the smoke tubes collected from a given sampling day, along with a field blank overlaid on the graph, with GC/MS detection. Blanks were collected prior to all disseminations. The concentrations of compounds varied between disseminations, depending on the total concentration in the sampling shed. Qualitative detection did not vary indicating that the compounds generated did not change. The identification of the compounds detected by GC/MS was accomplished using the spectral matching library of the Agilent Chemstation software. To acceptably conclude that a match had occurred, the mass spectral fragmentation pattern of an individual peak found in the sample had to have matched the compound fragmentation pattern stored in the spectral library with a qualifying index  $\geq 85\%$ . Benzene, toluene, ethyl benzene, xylene, styrene, naphthalene, chlorobenzene, phenol, benzaldehyde, benzofuran, benzonitrile, acetophenone, and benzene carboxylic acid are the compounds identified in the chromatograms for each disseminated grenade giving a qualifying index of  $\geq 85\%$ .

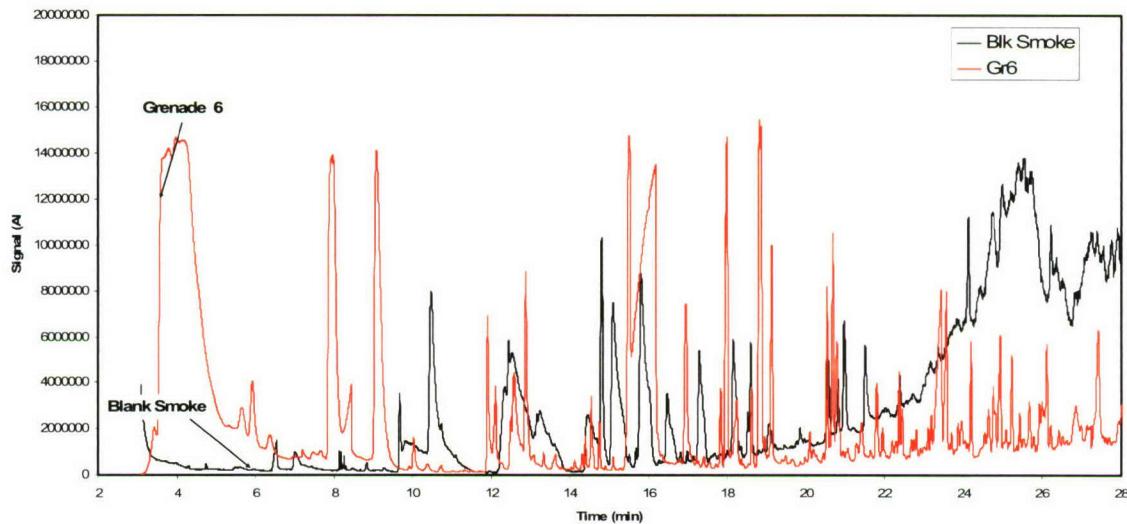


Figure 10. Chromatograms determined by GC-MS of vapor collection on sorbent tubes from dissemination of grenade #6 and of the blank vapor collected on the same day.

To assess the concentrations of several of these compounds, an EPA VOC (EPA VOC Mix 2, Supelco, Bellefonte, PA.) standard was used to quantitate the following compounds: benzene, toluene, ethylbenzene, xylene, styrene, and naphthalene. Figure 11 gives the calibration curves using linear regression for all the compounds mentioned over the range of 200 - 40 ng on the column detected by MS. Application of the measured area of the unknown smoke samples, to the equation of the line, allowed investigators to determine the concentration of the compounds found in each dissemination (collected on the tubes). All curves gave correlation coefficients,  $r^2 > 0.99$ . Table 6 gives the slope (m), average concentration in micrograms per liter and parts per million ( $n = 6$ ) for each compound quantitated from each dissemination. The calculation from microgram per liter to parts per million is accomplished using the following equation:  $(\mu\text{g/L}) (24.45) (\text{gas constant}) / (\text{gram molecular weight of substance})$ .

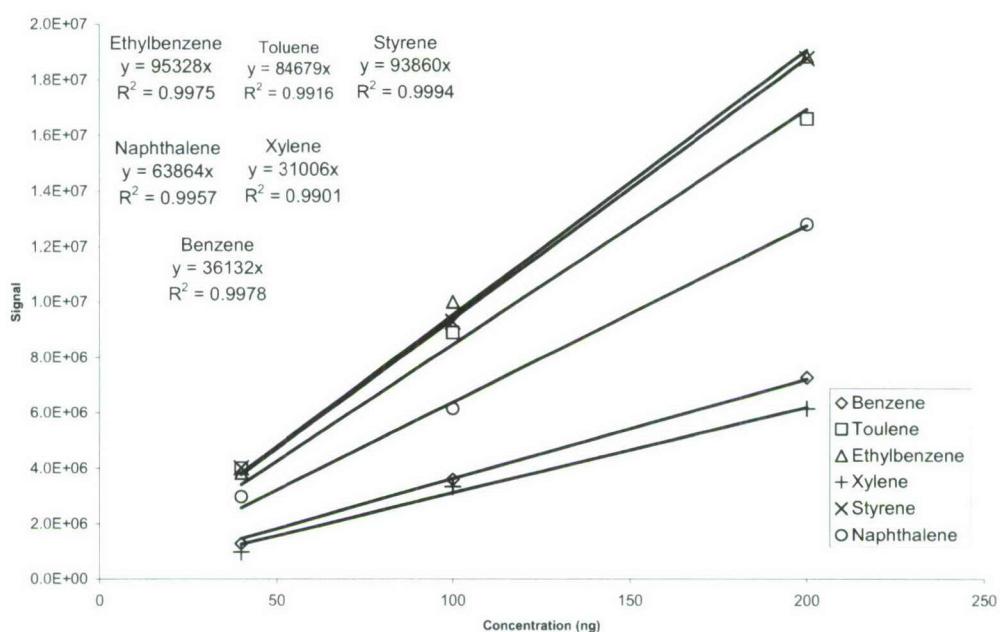


Figure 11. Calibration curves for ethylbenzene, toluene, styrene, naphthalene, xylene, and benzene determined by GC-MS using the EPA VOC (Mix #2) standard.

Table 6. Slope and concentration data for quantitated VOCs.

	Slope (m)	Average ( $\mu\text{g/L}$ )	Average (ppm)	Stdev (ppm)
Benzene	36132	1.8087	0.5662	0.2479
Toluene	84679	0.1624	0.0431	0.0404
Ethyl benzene	95328	0.0581	0.0134	0.0053
Xylene	31006	0.1203	0.0277	0.0212
Styrene	93860	0.3909	0.0918	0.0955
Naphthalene	63864	0.1490	0.0284	0.0409

### 3.4

#### Inorganic Gases

Smoke vapor collected in the large plastic jug was transferred to Tedlar bags and tested for inorganic gases. All the inorganic gases investigated from the disseminated 66mm RP grenades are given in Table 2. Carbon monoxide, CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>, NO/NO<sub>2</sub>, HCN, HCOH, and PH<sub>3</sub> (at a considerably lower concentration relative to the other inorganic gases detected) were the only inorganic gases identified in the disseminated smoke by the colorimetric detector tubes. Table 7 lists the average concentration and the SD (n = 7) for each of the inorganic gases determined in the smoke dissemination. Figure 12 gives the bar graph of the data collected and listed in Table 7, including error bars (measured as SD) for each average concentration. The SO<sub>2</sub> is an interferent in determining the level of HCN<sup>22</sup> using these tubes. Since the amount of interference can not be determined, the level for HCN is a range from the amount measured on the tube down to the worse case scenario of interferent caused by the SO<sub>2</sub>.

Table 7. Concentration of inorganic gases from smoke vapor determined by Kitagawa detector tubes.

Compound	Concentration (ppm)	SD
CO <sub>2</sub>	1986	515
CO	109	34
HCN	*24-30	7
HCOH	16	5
SO <sub>2</sub>	6	1
NO <sub>2</sub>	-	
NO	-	
NO <sub>x</sub>	85	13
PH <sub>3</sub>	0.021	0.003

\*HCN is a range due to interference caused by SO<sub>2</sub> concentrations<sup>22</sup>

### 3.5

#### Inorganic Anions

##### 3.5.1

##### Inorganic Anions - Standards and Calibration

An IC-CD was used to separate and detect anions of interest determined from GFF pads pulled during the smoke disseminations. For this study, four anions were investigated: Chloride (Cl), Nitrate (NO<sub>3</sub>), Phosphate (PO<sub>4</sub>), and Sulfate (SO<sub>4</sub>). Stock standard was used for calibration with concentrations provided by the manufacturer's certificate of analysis as 29.9, 100, 152, 150 mg/L, respectively. Calibration standards were prepared by making dilutions (10:1, 25:1, 50:1, 100:1, and 200:1) of the stock standard. Figure 13 gives a typical calibration curve, the equation of the line, and correlation coefficient for all four anions. Calibration curves were performed each day samples were ran. The limit of detection for each anion was determined to be 0.2, 0.006, 0.04, 0.03, and 0.006 mg/L for PO<sub>4</sub>, fluoride, SO<sub>4</sub>, nitrite, and NO<sub>3</sub>, respectively (s/n = 3).

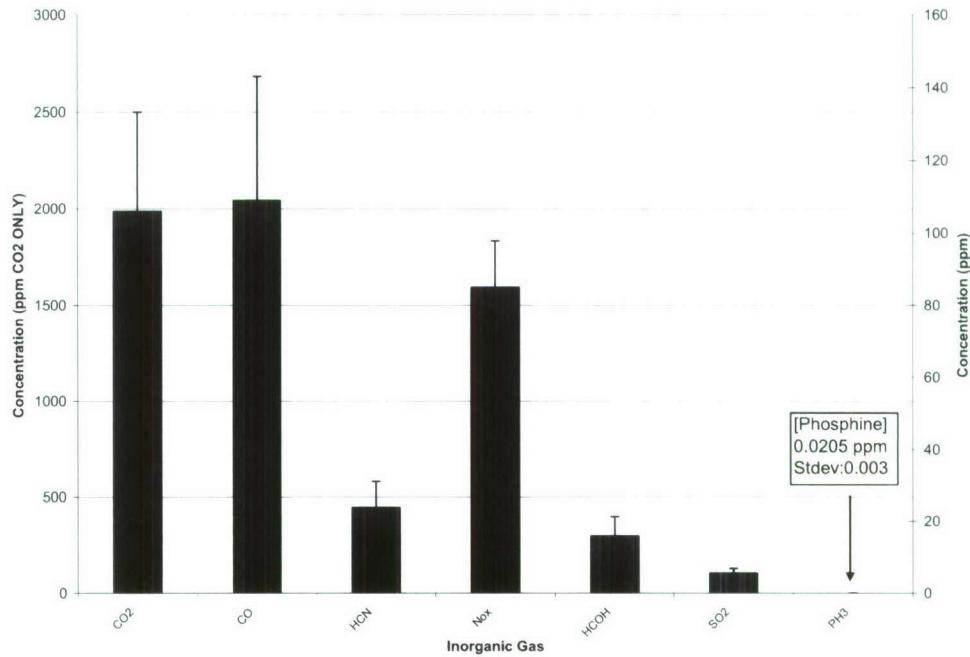


Figure 12. Average concentration of inorganic gases found in disseminated smoke from 66mm RP Grenades ( $n = 6$ ). Carbon dioxide concentration is given on the left scale with all other concentrations given on the right scale.

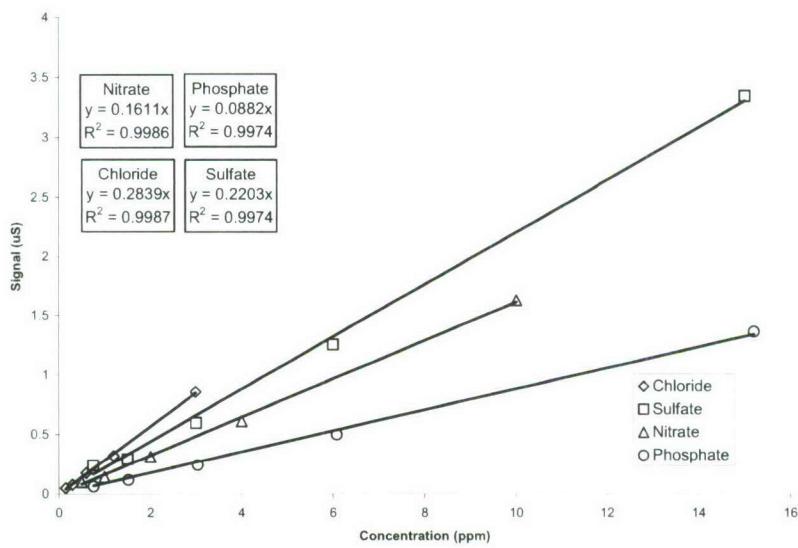


Figure 13. Calibration curves of four anions determined by IC-CD along with equation of lines and correlation coefficients ( $R^2$ ) for each anion.

### 3.5.2        Inorganic Anions - Percent Recoveries

Percent recoveries of PO<sub>4</sub> were measured by placing known concentrations of potassium phosphate (K<sub>3</sub>PO<sub>4</sub>) onto blank GFF pads following the sample preparation procedure given in Section 2.3.5.

Table 8. Percent recoveries of PO<sub>4</sub> from K<sub>3</sub>PO<sub>4</sub> determined by IC-CD.

Sample	K <sub>3</sub> PO <sub>4</sub> added (mg)	PO <sub>4</sub> (mg)	PO <sub>4</sub> (diluted) (ppm)	Experimental PO <sub>4</sub> (ppm)	Recovery (%)
1	13.84	6.19	3.54	3.03	85.72
2	36.74	16.44	3.76	3.12	83.08
3	28.84	12.90	2.95	2.54	86.16
4	41.2	18.43	4.21	3.68	87.40

Table 8 lists the amounts of K<sub>3</sub>PO<sub>4</sub> added to 50-mL conical vials containing blank GFF pads. The K<sub>3</sub>PO<sub>4</sub> samples were prepared IAW Section 2.3.5. Using stoichiometric calculations, the milligrams of PO<sub>4</sub> in the sample were determined and are listed in column 3. The samples were transferred to volumetric flasks and diluted 1:250 for sample #1 and 1:500 for samples 2 through 4. The fourth column lists the theoretical diluted concentrations of PO<sub>4</sub> in each sample. The samples were then run on the IC-CD, and the concentrations for each sample were determined (using linear regression from the calibration curves for PO<sub>4</sub>) as listed in column 5. The last column gives the percent recovery of PO<sub>4</sub> from K<sub>3</sub>PO<sub>4</sub> on GFF pads. The GFF pad blanks were prepared to assure the absence of interferents for phosphate by IC-CD, and none were found. The average percent recovery, SD, and %RSD determined for phosphate was 87.35% ± 3.1, 3.6, respectively (n = 14).

### 3.5.3        Inorganic Anions - Smoke Dissemination: Phosphoric Acid (H<sub>3</sub>PO<sub>4</sub>)

Phosphate was the main anion found in all the samples tested. The other anions investigated, (Cl, SO<sub>4</sub>, NO<sub>3</sub>), were not found in any appreciable amount in the test samples (>STEL, in ppm). For each grenade tested, three of the six GFF pads used for smoke sample collection were used to measure the amount of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) on each pad for each dissemination (n = 3 with a total of 7 grenades). Table 9 gives the average (n = 3) milligrams of PO<sub>4</sub> experimentally determined by IC-CD, the milligrams of H<sub>3</sub>PO<sub>4</sub> determined stoichiometrically, %H<sub>3</sub>PO<sub>4</sub>, and the concentration (milligrams per cubic meter) of H<sub>3</sub>PO<sub>4</sub> for all pads tested for each grenade.

Table 9. Percent H<sub>3</sub>PO<sub>4</sub> and aerosol concentration (mg/m<sup>3</sup>) determined from each dissemination (n = 3) by IC-CD.

Grenade	Experimental PO <sub>4</sub> (mg)	SD	Experimental H <sub>3</sub> PO <sub>4</sub> (mg)	SD	% H <sub>3</sub> PO <sub>4</sub>	SD	H <sub>3</sub> PO <sub>4</sub> (mg/m <sup>3</sup> )	SD
10/11/2007	16.83	0.55	17.36	0.57	59.60	1.07	33747.98	509.44
10/16/2007	21.99	1.63	22.69	1.68	49.93	1.24	42872.51	1596.12
10/18/2007	38.87	2.69	40.09	2.77	58.27	0.94	45414.66	996.76
10/23/2007	17.19	1.31	17.74	1.36	52.47	1.02	35479.45	1058.76
10/30/2007	16.11	0.74	16.62	0.77	57.41	1.32	33315.37	875.49
11/1/2007	20.82	2.33	21.60	2.40	53.34	0.58	43040.79	3467.13
11/6/2007	17.34	0.31	17.89	0.32	64.09	1.08	35357.29	1256.39

For each grenade, the second column gives the average milligrams of PO<sub>4</sub> found on the GFF pads as determined by IC-CD (n = 3). Using stoichiometry, the average milligram of H<sub>3</sub>PO<sub>4</sub> in the sample was calculated and is listed in column four. By dividing the milligrams of H<sub>3</sub>PO<sub>4</sub> determined on each GFF pad by the total weight found on each GFF pad sampled (data not shown), the %H<sub>3</sub>PO<sub>4</sub> on the pads was determined and is given in column six. By taking the mass of H<sub>3</sub>PO<sub>4</sub> determined by the IC-CD and dividing it by the volume of air (L) pulled on each pad (data not shown, approximately 0.5 L), the concentration (micrograms per liter or milligrams per cubic meter) of H<sub>3</sub>PO<sub>4</sub> can be calculated and is provided in the eighth column. From all the grenades, the average %H<sub>3</sub>PO<sub>4</sub> found on the GFF pads, SD, and %RSD determined by IC-CD was 56.45%, ± 4.8, %8.57 (n = 42). For all the grenades, the average concentration (milligrams per cubic meter), SD, and %RSD determined by IC-CD for H<sub>3</sub>PO<sub>4</sub> was 38,461.15 ± 5099.9, %13.3 (n = 42).

### 3.6 Metal Analysis-ICP-OES

#### 3.6.1 Metal Analysis - Standards and Calibration

Calibration standards were prepared from stock solutions of Mg, P, and K, which gave a certificate of analyses of 1000 µg/mL (ppm) for the concentration. Calibration standards for K and P were prepared by making dilutions in a 5% HCl//HNO<sub>3</sub> (aq) to yield concentrations of 100, 50, 25, 10, and 1 µg/mL and 10, 5, 1, 0.5, 0.1, and 0.05 µg./mL for Mg. Calibration curves for each element were prepared before every sample analysis. Calibration curves were subjected to linear regression analysis to determine concentrations of smoke dissemination solutions.

Table 10 gives example calibration curve data wavelength ( $\lambda$ , nm), slope (m), and correlation coefficient ( $R^2$ ) for each element tested by ICP-OES.

Table 10. Wavelengths (nm) and calibration data for all elemental metals detected by ICP-OES.

Element	$\lambda$ (nm)	m (slope)	$R^2$
Mg	280.271	3754272.17	0.99955
	279.553	8775412.84	0.99990
P	213.617	5868.46	0.99963
	214.714	2863.18	0.99964
K	766.49	77586.81	0.99978

### 3.6.2 Metal Analysis - Percent Recoveries

Percent recoveries for Mg, K, and P were determined by amending known concentrations of the oxide of each element onto blank GFF pads. The samples were prepared IAW the procedures for acid digestion given in Section 2.3.6.1, followed by analysis and quantitation by ICP-OES. Table 11 gives an example of the calculation of the percent recovery of phosphorous from sodium dibasic phosphate determined by ICP-OES. For all metals tested, the GFF pad blanks were prepared to assure the absence of interferents.

Table 11. Percent recoveries for P determined by ICP-OES.

Na <sub>2</sub> HPO <sub>4</sub> (mg)	PO <sub>4</sub> (mg)	P (mg)	Nominal P (ppm)	Experimental Con P (ppm) 213.617	Experimental Con P (ppm) 214.914	%Rec 213.617	%Rec 214.914
83.67	55.97	18.25	365.07	354.00	361.50	96.97	99.02
51.97	34.77	11.34	226.76	220.60	222.70	97.29	98.21
68.24	45.65	14.89	297.74	293.90	298.10	98.71	100.12

The first column lists the known milligram amounts of Na<sub>2</sub>HPO<sub>4</sub> added to 50-mL conical vials containing blank GFF pads. Using stoichiometric calculations, the milligrams of PO<sub>4</sub> and finally the elemental P in the sample were determined and are listed in columns two and three. The fourth column lists the theoretical concentrations of phosphorous in each 50-mL sample. The Na<sub>2</sub>HPO<sub>4</sub> samples were prepared IAW Section 2.3.6.1. The samples were run on the ICP-OES, and the concentrations for each sample were determined (using linear regression from the calibration curves for P) as listed in Table 12. The average percent recovery, SD, and %RSD determined for phosphorous at each wavelength was 97.65  $\pm$  0.9, %0.95 and 99.12  $\pm$  0.96, %0.97, respectively (n = 3 each).

The same calculations given above for elemental P were also used to calculate the percent recoveries for the other elements K from KOH and Mg from MgO as given in Tables 12 and 13, respectively.

Table 12. Percent recoveries for K determined by ICP-OES.

KOH (mg)	K (mg)	Nominal Con K (ppm)	Experimental Con K (ppm)	%Rec
94.21	55.79	1115.76	1000.00	89.62
103.61	61.35	1227.09	1187.00	96.73
101.58	60.15	1203.05	1121.00	93.18

Table 13. Percent recoveries for Mg determined by ICP-OES.

MgO (mg)	Mg (mg)	Nominal Mg Con (ppm)	Experimental Con (ppm) (279.553)	%Rec 279.553
2.58	1.56	31.12	25.34	81.43
7.66	4.62	92.39	82.70	89.52
9.98	6.02	120.37	108.00	89.73
25.83	15.58	311.53	281.55	90.38
53.58	32.31	646.22	584.30	90.42

From these experiments, the average percent recoveries, SDs, and %RSDs for each element at each wavelength were  $93.61 \pm 3.9$ , %4.2 (766.49 nm) ( $n = 6$ ) for K and  $82.62 \pm 4.3$ , %5.26 (280.271 nm) and  $82.14 \pm 8.3$ , %10.2 (279.553 nm) ( $n = 15$  each) for Mg.

### 3.6.3 Metal Analysis - Smoke Disseminations: H<sub>3</sub>PO<sub>4</sub>, KOH, and MgO

The composition of the 66mm RP grenade payload contains a large percentage of RP in the flares and pellets (>64%), indicating that the samples from the RP grenade should contain high concentrations of H<sub>3</sub>PO<sub>4</sub> followed by smaller concentrations of the other metals. As such, phosphorous was the first element investigated. Table 14 gives the average ( $n = 3$ ) experimental milligrams of P, the stoichiometrically determined milligrams of H<sub>3</sub>PO<sub>4</sub>, the percent H<sub>3</sub>PO<sub>4</sub> on GFF pad, and finally the concentration (milligrams per cubic meter) of H<sub>3</sub>PO<sub>4</sub> for each grenade dissemination.

For each grenade given in Table 14, the second column lists the average milligrams of P ( $n = 3$ ) found on the GFF pads determined by ICP-OES (using linear regression from the calibration curves for P). Using stoichiometry, the average milligrams of H<sub>3</sub>PO<sub>4</sub> in the sample were calculated and are listed. By dividing the milligrams of H<sub>3</sub>PO<sub>4</sub> determined on each GFF pad by the total weight pulled onto each GFF pad sampled (data not shown), the percent of H<sub>3</sub>PO<sub>4</sub> on the pads was determined and is given. Finally, by taking the mass of H<sub>3</sub>PO<sub>4</sub> and dividing it by the volume of air (L) pulled on each pad, the concentration of H<sub>3</sub>PO<sub>4</sub> (micrograms per liter or milligrams per cubic meter) can be calculated. The average concentration (milligrams per cubic meter) of H<sub>3</sub>PO<sub>4</sub> determined for each dissemination/grenade is listed. For all the grenades, the average percent H<sub>3</sub>PO<sub>4</sub> found on the GFF pads, SD, and %RSD determined

by ICP-OES was  $65.66 \pm 9.87$ , %15.0 (n = 42). For all the grenades, the average concentration (milligrams per cubic meter), SD, and %RSD determined by ICP-OES for  $\text{H}_3\text{PO}_4$  was  $43,144.27 \pm 5171.3$ , 11.99% (n = 42).

Table 14. Experimental amount of P, %  $\text{H}_3\text{PO}_4$ , and  $\text{H}_3\text{PO}_4$  concentration determined from each dissemination (n = 3) by ICP-OES. ( $\sigma$  - SD).

Grenade	Experimental P (mg)	Experimental $\text{H}_3\text{PO}_4$ (mg)	% $\text{H}_3\text{PO}_4$	Concentration (mg/m <sup>3</sup> )
10/11/2007	6.24	19.75	72.17	38860.06
$\sigma$	0.25	0.8	2.2	1183.3
10/16/2007	7.61	24.09	56.43	47469.69
$\sigma$	0.25	0.8	0.5	597.3
10/18/2007	9.03	28.58	43.53	34161.68
$\sigma$	0.29	0.9	2.0	447.8
10/23/2007	8.14	25.77	66.06	48022.64
$\sigma$	0.71	2.2	1.1	1716.7
10/30/2007	6.79	21.49	68.03	39873.88
$\sigma$	0.60	1.9	1.5	1241.4
11/1/2007	7.61	24.09	67.41	48475.18
$\sigma$	0.33	1.0	1.0	3136.6
11/6/2007	7.27	23.01	77.74	42166.33
$\sigma$	0.64	2.0	1.7	1039.2

The next metal found in the smoke aerosol was potassium (K). For this element, it was hypothesized that the most probable oxide formed from the combustion of K would be potassium oxide ( $\text{K}_2\text{O}$ ), and upon reaction with water vapor in the air would form KOH.<sup>23</sup> As such, the following data listing and calculations were tailored for this element/oxide consideration. Table 15 gives the average (n = 3) experimental milligrams of K, the stoichiometrically determined milligrams of KOH, the percent KOH, and finally the concentration (milligrams per cubic meter) of KOH determined for each grenade dissemination.

For K, the same calculations for P are applied here. For each grenade given in Table 15, the second column lists the average milligrams of K found (n = 3) on the GFF pads determined by ICP-OES (using linear regression from the calibration curves for K). From all the grenades, the average percent KOH found on the GFF pads, SD, and %RSD determined by ICP-OES was determined to be  $2.300 \pm 0.395$ , %17.1 (n = 42). For all the grenades, the average concentration for KOH (milligrams/cubic meter), SD, and %RSD determined by ICP-OES was  $1509.69 \pm 166.0$ , %11.0 (n = 42).

Finally, the third metal found in the smoke aerosol was magnesium (Mg). For this element, it was determined that the most probable oxide formed from the combustion of Mg would be MgO. As such, the calculations were tailored for this element/oxide consideration.

Table 15. Experimental amount of K, KOH, %KOH, and KOH concentration found in each dissemination as determined by ICP-OES. ( $\sigma$  - SD)

Grenade	Experimental K (mg)	Experimental KOH (mg)	%KOH	Concentration (mg/m <sup>3</sup> )
10/11/2007	0.453	0.650	2.376	1298.39
$\sigma$	0.013	0.019	0.078	38.20
10/16/2007	0.620	0.890	2.084	1753.03
$\sigma$	0.018	0.026	0.034	23.02
10/18/2007	0.732	1.051	1.599	1256.03
$\sigma$	0.021	0.031	0.047	32.69
10/23/2007	0.571	0.819	2.099	1526.19
$\sigma$	0.056	0.080	0.035	58.65
10/30/2007	0.532	0.763	2.416	1415.89
$\sigma$	0.048	0.069	0.053	40.72
11/1/2007	0.560	0.804	2.249	1617.94
$\sigma$	0.026	0.038	0.026	107.99
11/6/2007	0.619	0.888	2.999	1626.51
$\sigma$	0.058	0.083	0.064	39.88

Table 16 gives the average ( $n = 3$ ) experimental milligrams of Mg, the stoichiometrically determined milligrams of MgO, the %MgO, and finally the concentration (milligrams per cubic meter) of MgO for each grenade dissemination ( $n = 3$ ).

Table 16. Experimental Mg, MgO, %MgO, and MgO concentration found in each dissemination as determined by ICP-OES. ( $\sigma$  - SD)

Grenade	Experimental Mg (mg)	Experimental MgO (mg)	MgO (%)	Concentration (mg/m <sup>3</sup> )
10/11/2007	0.133	0.221	0.808	435.23
$\sigma$	0.0048	0.0079	0.033	14.9
10/16/2007	0.148	0.245	0.575	483.64
$\sigma$	0.0031	0.0052	0.019	13.0
10/18/2007	0.202	0.335	0.509	400.01
$\sigma$	0.0078	0.013	0.017	15.5
10/23/2007	0.155	0.257	0.658	478.29
$\sigma$	0.0132	0.022	0.025	15.9
10/30/2007	0.145	0.241	0.764	447.97
$\sigma$	0.0116	0.019	0.013	9.5
11/1/2007	0.145	0.241	0.674	484.52
$\sigma$	0.0036	0.006	0.02	24.8
11/6/2007	0.168	0.278	0.942	510.68
$\sigma$	0.0130	0.021	0.018	10.4

The same calculations for P are applied again for Mg. From all the grenades, the average %MgO found on the GFF pads, SD, and %RSD determined by ICP-OES was  $0.7168 \pm 0.135$ , %18.8 (n = 42). For all the grenades, the average concentration for MgO (milligrams per cubic meter), SD, and %RSD determined by ICP-OES was  $466.78 \pm 36.7$ , %7.9 (n = 42).

### 3.7

#### Long-Term Storage of the 66mm RP Grenades

##### Long-Term Storage-Sampling Over 12 Weeks

Figure 14 depicts the %RH (bottom line, blue) and the temperature (top line, red) over the 12-week period. The RH and temperature remained constant throughout the 12-weeks. The RH trace does show signs of two spikes in humidity. This was due to drying of the wet bulb wick, causing the readout device to artificially read a higher RH, meaning that the RH was stable minus artificial changes.

Figure 15 gives the graph depicting the PH<sub>3</sub> measured inside the dead space of two ammunition cans over the period of the study. The data collected for the PH<sub>3</sub> off gassing was taken from the Kitagawa detector tubes. For the first 4 weeks of the study, GC-FID was used to measure PH<sub>3</sub> as well. This process had to be stopped due to the discovery of unforeseen problems with the GC-FID that dated back to the beginning of the analysis, so reported data is limited to the detector tubes. Samples were pulled for the weeks of 12/26/07 and 1/2/08 for Kitagawa tube and FID analysis; but, due to problems with sampling and analysis, both samples were lost.

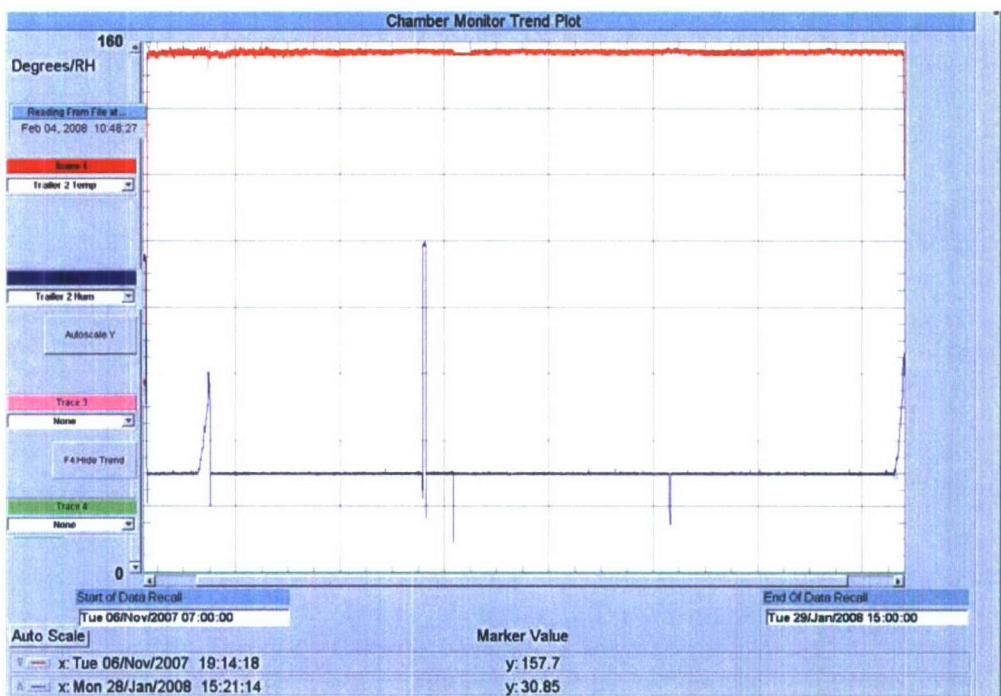


Figure 14. %RH (blue) and temperature (F) (red) over the course of the 12-week storage period.

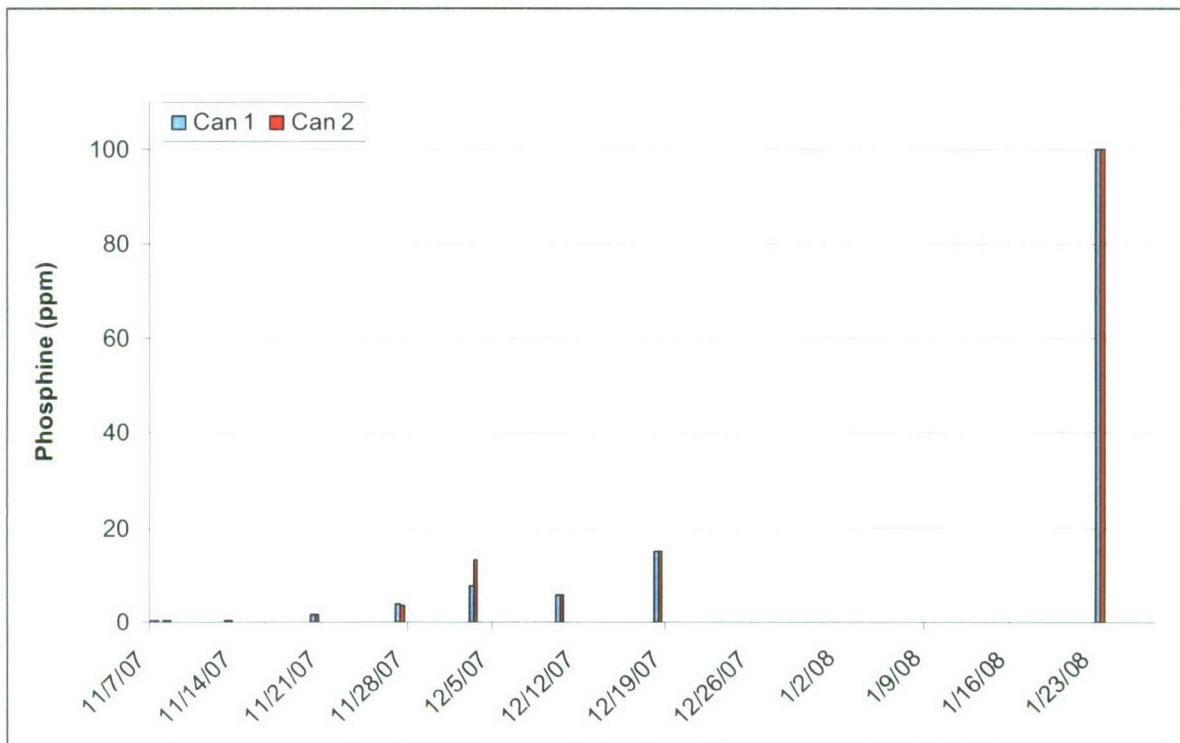


Figure 15. PH<sub>3</sub> off-gassing over the course of the 12-week accelerated aging test.

At the end of the 12-week study, three ammunition cans were also placed inside the climatically controlled chamber for sampling. These three cans were used to determine the final concentration of PH<sub>3</sub> in the ammunition cans following the accelerated aging test. The concentration of PH<sub>3</sub> determined in the gas collected from inside the ammunition cans, was 400, 50, and 200 ppm. The concentration of the PH<sub>3</sub> was also determined by Kitagawa detector tubes.

Following the sampling, the four ammunition cans, 16 grenades in all, were taken down range and systematically set off to test for functionality. Functionality was assessed on a pass fail basis being: pass - the grenade functioned properly (fired), or failed - the grenade did not function properly (did not fire). Each grenade passed the functionality testing even after being subjected to the long-term storage conditions.

### 3.8 Aquatic Toxicity Testing

Ceriodaphnia growth media (20% Perrier water and 80% RO water) was the solution used to produce the smoke aerosol and residue extracts. The resulting pH of the smoke aerosol extract at a nominal concentration of 3,313.3 mg/L (100% extract) was 2.5. The resulting pH of the smoke residue extract at a nominal concentration of 3,000 mg/L (100% extract) was 6.8. The extracts were serially diluted to produce the treatment groups used in toxicity testing. In Figure 16, the pH of the smoke aerosol and residue treatment groups are graphically displayed.

#### 3.8.1 Microtox Assay

The 5- and 15-min nominal EC<sub>50</sub> values for smoke residue extract toxicity to *Vibrio fischeri* was >3,000 mg/L (highest concentration tested, Table 17). The pH during the smoke residue extract toxicity testing ranged from 6.1 for the control to 6.8 for the 3,000-mg/L treatment group (Figure 16). The smoke aerosol extract testing had a pH range from 6.1 for the control to 2.5 for the 3,313.3 mg/L treatment group (Figure 16). The 5- and 15-min nominal EC<sub>50</sub> values for the smoke aerosol extract were 15.4 and 16.2 mg/L, respectively. However, when the smoke aerosol extract was pH adjusted, the extract EC<sub>50</sub> > 3,313.3 mg/L.

Table 17. Microtox test results from exposures to 66mm RP smoke aerosol and residue extract. The pH adjustments to aerosol extract eliminated toxicity up to the highest concentration tested.

Microtox Test Results			
	Aerosol Extract (mg/L)	Aerosol Extract pH Adjusted (mg/L)	Residue Extract (mg/L)
EC <sub>50</sub> (5 min)	15.4 (6.5-36.6)*	>3,313.3	>3,000.0
EC <sub>50</sub> (15 min)	16.2 (5.9-44.5)*	>3,313.3	>3,000.0

\*95% Confidence Interval

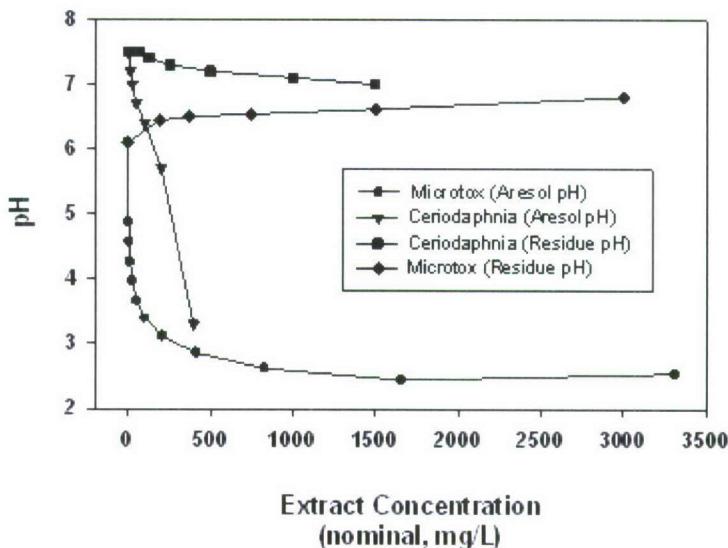


Figure 16. Extract pH of treatment groups during the microtox and ceriodaphnia testing.

Zinc sulfate ( $\text{ZnSO}_4 \times 7\text{H}_2\text{O}$ ) was used as the reference standard to confirm the viability of the microtox bacteria, *Vibrio fischeri*. The QA/QC toxicity results fell within the acceptable toxicity  $\text{EC}_{50}$  range (between 3 and 10 mg/L) for a 5-min exposure.

### 3.8.2 Ceriodaphnia Assay

The smoke aerosol extract was not pH adjusted for use in the 7-day chronic ceriodaphnia toxicity test because there were significant effects at concentrations below pH effects. The pH recorded during the 7-day chronic tests with smoke aerosol extract ranged from 7.5 for the control to 3.3 for the 400-mg/L extract (Figure 16). There was 100% mortality within the first 24 hr of exposure to the 400-mg/L extract (highest concentration used in chronic testing), with no mortality recorded in treatment groups 0, 12.5, 25, 50, 100, and 200 mg/L for the remainder of testing. The NOEC for survival was 200 mg/L, and the NOEC for reproduction was 12.5 mg/L. The LOEC for survival and reproduction was 400 and 25 mg/L, respectively (Table 18 and Figure 17). The 7-day  $\text{IC}_{50}$  and  $\text{IC}_{20}$  were 103.1 and 12.8 mg/L.

The 24-hr acute ceriodaphnia test using smoke aerosol extract resulted in an  $\text{EC}_{50} = 225.3$  mg/L. When the pH of the aerosol extract was adjusted, the resulting 24-hr  $\text{EC}_{50} = 1,648$  mg/L (7.3 x reduction in toxicity).

The smoke residue extract did not exhibit pH effects during the 7-day chronic ceriodaphnia testing. The pH during testing ranged from 7.5 for the control to 7.1 for the 1500 mg/L extract (highest concentration used in chronic testing, Figure 18). After 7 days of exposure, there was 40% mortality in the highest treatment group (1,500 mg/L), and no mortality recorded in the remainder of the treatments (0, 62.5, 125, 250, 500, and 1000 mg/L). The NOEC for survival was >1,500 mg/L, and the NOEC for reproduction was 125 mg/L. The LOEC for survival and reproduction was >1,500- and 250-mg/L extract, respectively (Table 18 and

Figure 18). The 7-day IC<sub>50</sub> and IC<sub>20</sub> were 214.3 mg/L and 115.8 mg/L, respectively. The 24-hr acute ceriodaphnia test using smoke residue extract resulted in an EC<sub>50</sub> = 2,616 mg/L.

Table 18. Ceriodaphnia test results from exposures to 66mm RP smoke aerosol and residue extracts.

Ceriodaphnia Test Results		
	Aerosol Extract (mg/L) (95% Confidence Interval)	Residue Extract (mg/L) (95% Confidence Interval)
EC <sub>50</sub> (24 hr)	225* 1,648 (pH adjusted extract)	2,616 (2,381-2,868)
7D NOEC (survival)	200	1,500
7D LOEC (survival)	400	> 1,500
7D NOEC (reproduction)	12.5	125
7D LOEC (reproduction)	25	250
7D IC <sub>20</sub>	12.8 (6.1-23.6)	115.8 (48.5-179.7)
7D IC <sub>50</sub>	103.1 (22.3-133.1)	214.3 (169.0-307.0)

\*Could not be determined

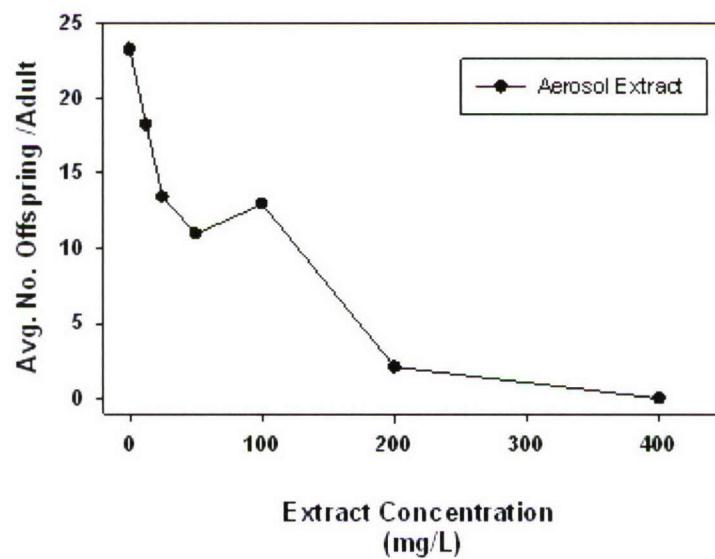


Figure 17. Offspring production in the 7-day chronic toxicity test using aerosol extract.

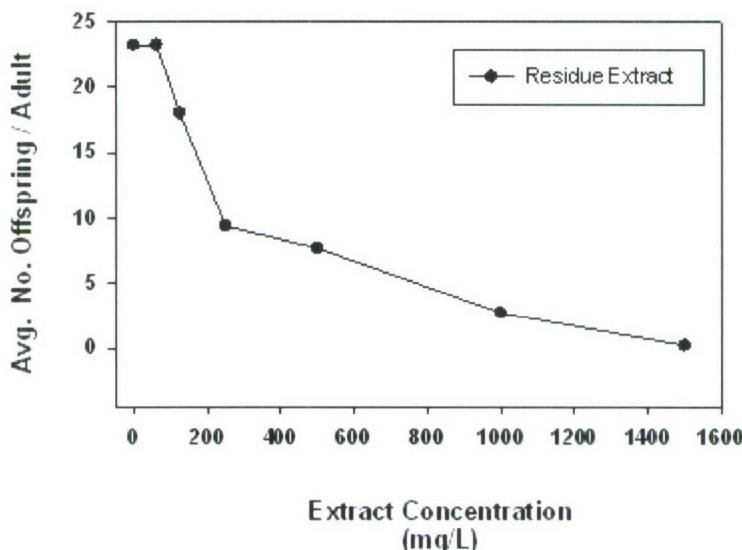


Figure 18. Offspring production in the 7-day chronic toxicity test using residueextract.

The control ceriodaphnia met the EPA test acceptability criteria of  $\geq 80\%$  survival and producing an average of 15 or more young per adult.

#### 4. DISCUSSION

Historically, obscurants have been important to the military in various applications. The creation and development of safe and effective smokes and obscurants is of great importance to the U.S. military. One important point to emphasize is that there is no smoke formulation that is totally non-toxic. The role of development is to create the “safest” smoke formulation possible that would retain operational efficiency.

The current study for the combustion product and chemical characterization testing for the 66mm RP Smoke Screening Vehicle Launched MK1 MOD0 was accomplished in a dynamic system inside an enclosed shed. The experimental design did not implement strict controls to maintain either a stable or uniform concentration within the shed. In this scenario, the disseminated smoke cloud would be concentrated by enclosing it in the sampling shed so the overall smoke concentration would be expected to be higher than in an open air dissemination of the same device.

##### 4.1 Shed Concentrations

The grenade was being disseminated outside of a controlled environment, so the concentration varied from run to run. The average concentration was  $68,132.19 \pm 11,497 \text{ mg/m}^3$ , which gave a range of  $56,635.19$  to  $76,629.19 \text{ mg/m}^3$ . Table 4 lists the average aerosol concentrations ( $n = 6$  for each dissemination) for all the disseminations as well as their respective

temperature (°F) and RH (%RH). These experiments were conducted in autumn-to-winter weather of the northeastern United States. The temperature in °F, and RH ranged from 42 to 69.3 °F and 66.45 to 100% RH, respectively, throughout the testing. The formation of the aerosol for RP is highly dependent on RH (amount of water vapor in the air) and the temperature. Figure 9 gives the bar graph of the data listed in Table 4 with the aerosol concentration (milligrams per cubic meter) on the left axis and the T and %RH on the right axis. By looking at Figure 9, it becomes apparent that the fluctuations in the ambient temperature and humidity can affect the output of the RP grenade, while some deviations in device performance may have also been observed. A general trend can be observed that when temperature and RH increase, the total output of smoke aerosol formed seems to increase (within statistical tolerances for grenades 1-3). On days when temperature increased but the RH either stayed stagnant or decreased, or when temperature increased but the RH increased, the correlation becomes more complicated, and the performance output trend is lost.

#### 4.2 Particle Size

Two separate impactors were used on four of the disseminations at two different times (60-90 s and 240-270 s following bursting) to ascertain if the particle size of the aerosol would change over the course of the dissemination. Table 5 lists all the particle size data, including the MMAD,  $\sigma_g$ , and the percent respirable mass determined for all the impactors collected for each 66mm RP grenade dissemination. The average MMAD,  $\sigma_g$ , and the percent respirable mass over all the times and disseminations were  $3.743 \pm 0.58$ ,  $1.978 \pm 0.16$ , and  $50.591 \pm 6$ , respectively. The particle size of the aerosol increased over the course of the dissemination as indicated by the MMAD of  $3.444 \pm 0.35$  at 60-90 s; whereas, for the 240- to 270-s sample, it was  $4.185 \pm 0.56$ . The larger particle size could be attributed to possible agglomeration due to the relatively high smoke concentration inside the shed, or due to the hydrophilic nature of the aerosol. The dissemination of the smoke grenade inside the shed does not represent a real world scenario. As such, an open air dissemination was initiated down wind of activation of a grenade to determine particle size. The measurement of the particle size over the course of the dissemination of the 66mm RP grenade in the open air, down wind dissemination (Section 3.2.2) gave an MMAD and  $\sigma_g$  of  $1.032 \pm 0.06$  and  $1.332 \pm 0.03$ , ( $n = 6$ ), respectively, with a respirable mass of 99.201%. The sampling was done over 60 s at 10 s/sample. This MMAD and  $\sigma_g$  indicates that the particle size should be  $\leq 1 \mu\text{m}$  in an open air dissemination, which more closely resembles a real world scenario for the use of the grenade. The MMAD and  $\sigma_g$  more closely compare to the particle size data found by RWM.<sup>12,24</sup>

Under the conditions of this test, 99.2% of the particles were respirable. The ACGIH defines these particles as those that are deposited in the gas exchange alveolar region of the lung.<sup>14</sup> This implies that the particles will likely undergo impaction in the alveolar portion of the lower respiratory system.<sup>25</sup> With this particle size, it is likely that diffusion mechanisms at the blood barrier will not occur; but, deep deposition into the respiratory system is still probable.

## 4.3

VOCs

As Figure 10 indicates, several VOCs were found in the disseminated smoke. Qualitative detection did not vary, indicating that the same compounds appeared consistently for each dissemination. Only the concentrations of compounds varied between disseminations, depending on the total concentration present in the sampling shed as indicated by Table 6. The smoke payload not only contained metals (P, KNO<sub>3</sub>, Mg, other igniter and bursting charges, and delay elements), but the payload also contained binder, which is organic in composition. Naphthalene was the only polyaromatic hydrocarbon observed in the smoke vapor.

Table 19. Slope and average concentration (n = 6) for each VOC investigated.

	Slope (m)	Average ( $\mu\text{g/L}$ )	Average (ppm)	Stdev (ppm)	TLV-TWA* (ppm)	STEL* (ppm)
Benzene	36132	1.8087	0.5662	0.2479	0.5	2.5
Toulene	84679	0.1624	0.0431	0.0404	50	
Ethyl benzene	95328	0.0581	0.0134	0.0053	100	125
Xylene	31006	0.1203	0.0277	0.0212	100	150
Styrene	93860	0.3909	0.0918	0.0955	20	40
Naphthalene	63864	0.1490	0.0284	0.0409	10	15

\*References (MSDS, TLV, and BEIs ACGIH Worldwide Signature Publications)

The presence of binder to the combustible payload composition mechanism for smoke dissemination is a possible explanation for the high number of aromatic hydrocarbons found in the vapor of the disseminated smoke. Table 19 lists the compounds that were detected and quantitated using GC/MS detection. The table also lists the TLV-TWA and STEL (given in the ACGIH reference for TLVs)<sup>14</sup> for each compound detected. This reference acts as a guideline for the assessment of safe levels of exposure to various chemical agents and substances that could pose a potential health hazard. All the compounds given in Table 20 have concentrations less than their respective STELs. Also, investigators must consider that the concentrations in these experiments are higher than would be expected in real world application of this munition due to concentration of the disseminated smoke sample in the shed. It is possible that other compounds could also be formed during dissemination; but, our observations seem to indicate that the VOCs formed are relatively low in concentration, even though this cannot be proven without a specific study looking for the formation of an individual chemical.

## 4.4

Inorganic Gases

Following disseminations, air samples were analyzed for inorganic gases considered to be of toxicological concern. Table 20 lists the inorganic gas, the concentration determined, SD, the TLV-TWA, the STEL, and possible toxicological effects of the inorganic gases detected. The values are those listed by ACGIH.<sup>14</sup> The CO<sub>2</sub> levels were less than the TLV-TWA and the STEL. Carbon monoxide was 4 times greater than the established TLV-TWA. The HCN concentration was greater than the Short Term Exposure Limit – Ceiling (STEL-C). Formaldehyde levels were much higher than the respective STEL. Sulfur dioxide

levels were slightly higher than its respective STEL and 6 times as high as the TLV-TWA given by the ACGIH. The NO<sub>x</sub> tubes are an EPA standard that simultaneously measures for nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>). During combustion processes, the primary pollutant is the free radical form of NO. Usually, NO converts to NO<sub>2</sub> in tens of minutes. By the time the air was sampled, most of the NO<sub>x</sub> was probably NO<sub>2</sub>. If this is considered, then the NO<sub>x</sub> ≈ NO<sub>2</sub> levels were higher than the TLV-TWA for NO<sub>2</sub>.

Table 20. Concentration determined in the 66mm RP disseminated smoke as well as TLV-TWA, STEL (ppm) and toxicological effects of the inorganic gases.

Compound	Concentration (ppm)	SD	TLV-TWA* (ppm)	STEL* (ppm)
CO <sub>2</sub>	1986	515	5000	30000
CO	109	34	25	400
NO <sub>x</sub>	85	13	50	5
HCN	^24-30	7	4.7	C 4.7
HCOH	16	5	1	0.3
SO <sub>2</sub>	6	1	0	5
PH <sub>3</sub>	0.021	0.003	0.3	1

<sup>a</sup>HCN is a range due to interference caused by SO<sub>2</sub> concentrations<sup>22</sup>

\*Taken from the TLVs and BEIs of the ACGIH.

#### 4.5 Inorganic Anions and Metals

All the sample preparation for the inorganic anions (water extraction) and the metals (acid digestion) was appropriate and gave percent recoveries  $\geq 82\%$  for all anions and metals investigated. The calibration of the IC-CD and the ICP-OES was linear ( $R^2 > 0.999$ ) for all analytes investigated and was consistent over the entire sampling period (data not shown). Table 21 lists the percent of each anion and metal found on the GFF sampling pads with Table 22 giving the concentration averaged over all disseminations ( $n = 42$ ) determined by ICP-OES and IC-CD.

The mean concentration of phosphate (principally in the form of phosphoric acid) calculated over all disseminations by ICP-OES was 43,144.27 ppm with an SD of 5171.3 ppm. For the IC-CD, the average concentration was 38,461.15 with an SD of 5,099.9. The overall range was 37,972.97 – 48,315.57 ppm and 33,361.25 – 43,561.05 ppm for ICP-OES and IC-CD, respectively. Although both ranges are much higher than the established TLV (1 mg/m<sup>3</sup>)<sup>26</sup> for H<sub>3</sub>PO<sub>4</sub>, the presence of high amounts of H<sub>3</sub>PO<sub>4</sub> in these smokes must be expected. However, even with dissipation, the high concentrations observed in the fine particle smoke could still induce an irritancy effect in personnel. This effect is common with all RP-based smokes. The concentrations of H<sub>3</sub>PO<sub>4</sub> found on the GFF pads by either IC-CD or ICP-OES was significantly

different at the 95% confidence level. Statistical analysis was done by applying the Mann-Whitney t-test to the data determined by IC-CD and ICP-OES.

Table 21. Average percent weight determined for H<sub>3</sub>PO<sub>4</sub>, KOH, and MgO.

Anion/Metal	IC H <sub>3</sub> PO <sub>4</sub> (%)	ICP-OES H <sub>3</sub> PO <sub>4</sub> (%)	ICP-OES KOH (%)	ICP-OES MgO (%)
Average	56.45	65.66	2.300	0.7168
SD	4.8	9.9	0.395	0.135
%RSD*	8.6	15.0	17.1	18.8

\*RSD, n = 42

Table 22. Average concentration determined for H<sub>3</sub>PO<sub>4</sub>, KOH, and MgO.

Anion/Metal	IC H <sub>3</sub> PO <sub>4</sub> (mg/m <sup>3</sup> )	ICP-OES H <sub>3</sub> PO <sub>4</sub> (mg/m <sup>3</sup> )	ICP-OES KOH (mg/m <sup>3</sup> )	ICP-OES MgO (mg/m <sup>3</sup> )
Average	38,461.15	43,144.27	1509.69	466.78
SD	5099.9	5171.3	166.0	36.7
%RSD*	13.3	12.0	11	7.9

\*RSD, n = 42

As Table 22 indicates, the percent H<sub>3</sub>PO<sub>4</sub> found on the GFF pads was >56 and 65% of the total weight for all disseminations determined by IC-CD and ICP-OES, respectively. These values were found by RWM.<sup>25</sup> The percent of H<sub>3</sub>PO<sub>4</sub> found on the GFF pads by IC-CD and ICP-OES was significantly different at the 95% confidence level. Statistical analysis was done by again applying the Mann-Whitney t-test to the data determined by IC-CD and ICP-OES.

The differences in the percent recoveries and milligrams per cubic meter for H<sub>3</sub>PO<sub>4</sub> determined by IC and ICP-OES are not significantly different. In part, this is due to the high SDs of the overall experiment most likely due to the dynamic system of the test (no equilibration of the smoke inside the shed) as well as the differences in the temperature and RH from day to day. However, the consistently higher percent recoveries and concentrations (milligrams per cubic meter) of the H<sub>3</sub>PO<sub>4</sub> determined by ICP-OES compared to those of IC could be attributed to the presence of other phosphorous oxides (i.e., phosphorous pentoxide) in the sampling matrix (of the GFF pad). These other phosphorous oxides may be present due to incomplete conversion of RP to the P<sub>2</sub>O<sub>5</sub> and/or incomplete chemisorption of P<sub>2</sub>O<sub>5</sub>, which upon interaction with water would form H<sub>3</sub>PO<sub>4</sub>.<sup>10</sup> The sample preparation and introduction methods of the ICP-OES allow detection of all P-containing analytes. Unfortunately, this method does not identify the oxidized species of the P element prior to or after detection. The IC-CD only provides concentration of the PO<sub>4</sub> molecule, leading to the incorrect observation of more P by ICP-OES.

As for the other metals tested, KOH and MgO were  $2.300\% \pm 0.395$  and  $0.7168\% \pm 0.135$ , respectively, of the total weight of the GFF pads over all the disseminations. The KOH gave an average concentration of  $1509.69 \pm 166.0$  mg/m<sup>3</sup> for all disseminations. This gives a concentration range for KOH as 1343.69 to 1675.69 mg/m<sup>3</sup>. It has been suggested that the combustion of K would form K<sub>2</sub>O, which upon interaction with water vapor in the air reacts fairly strongly to form KOH.<sup>23</sup> Potassium hydroxide was chosen as the form or oxide species most likely expected for K in the smoke samples collected. The concentration of KOH determined for the 66mm RP grenades is much higher than the STEL-C of 2 mg/m<sup>3</sup> as given by ACGIH. As for MgO, the average concentration determined for all disseminations was  $466.78 \pm 36.7$  mg/m<sup>3</sup>. This gives MgO a concentration range of 503.48 – 430.08 mg/m<sup>3</sup>, which is much higher than the TLV-TWA of 10 mg/m<sup>3</sup> given by the ACGIH. Due to the nature of the pyrotechnic payload, it was expected that potassium and magnesium would be in the smoke aerosol in fairly high concentrations.

#### 4.6 Long-Term Storage Tests

The accelerated aging test was conducted on the RP 66mm grenades to investigate the possibility of phosphine off gassing during a long-term storage scenario. By using the Arrhenius relationship, an accelerated long-term storage study was accomplished using elevated temperatures (higher than ambient). In this experiment, 12 weeks at 158 °F (70 °C) at 30% RH was used to simulate 5 years of storage.<sup>19</sup> The disadvantages of using higher temperatures to simulate aging is that higher temperatures often increase chemical reaction rates and/or introduce chemical reactions that may or may not occur without adding energy (heat). Even so, higher temperature, accelerated aging tests are the only current mechanisms of accelerating aging studies.

With many of the RP munitions, phosphine evolution is a known phenomenon that occurs during storage due to an RPs tendency to react with water in the air to form PH<sub>3</sub> according to the following equation:  $2P_4 + 12 H_2O \rightarrow 5PH_3 + 3H_3PO_4$ .<sup>10</sup> Phosphine is toxic and considered an inhalation hazard. The current 60-min LC<sub>50</sub> value for phosphine is 20 ppm with the lower explosive limit (LEL) of phosphine being 1.6% (16,000 ppm).<sup>27</sup> Phosphine may also accumulate in confined spaces, i.e., ammunition cans and bunkers as well as storage units with high enough concentrations creating an inhalation hazard.

Figure 14 gives the concentration of phosphine determined from the dead space inside the ammunition cans sampled over the 12-week period of the accelerated aging test. Figure 14 shows that phosphine evolved from the 66mm RP grenades and increased in concentration over time. At the start of the 3<sup>rd</sup> week of sampling from the ammunition cans, the PH<sub>3</sub> concentration found was greater than the 0.3-ppm STEL. The large increase in PH<sub>3</sub> concentration found in the ammunition cans as shown in Figure 14 is attributed to the increased amount of time between sampling at the end of the experiment. The time between the two last samples was approximately 1 month. Removing the gas from the ammunition cans, sampled over the 12-week period, not only removed some of the PH<sub>3</sub> that was already present, but it also added dilution air to the total volume of the ammunition can. The diluted air could have ultimately lowered the PH<sub>3</sub> concentration found in the ammunition cans at the end of the experiment. This could explain why the concentration of PH<sub>3</sub> was lower in the sampled

ammunition cans compared to the PH<sub>3</sub> concentration determined in the three untouched ammunition cans at the end of the experiment. In the end, the sampled cans would have less PH<sub>3</sub> present than the untouched cans.

The final concentrations of PH<sub>3</sub> determined from the dead space inside the ammunition cans that were untouched over the 12-week aging test were 400, 50, and 200 ppm. The reason for the difference in the concentrations can be attributed to improper sampling from the ammunition cans. The first can had the first hole drilled and sealed with a rubber stopper. The second hole was drilled, and the sample was pulled with proper connections to the hose barb and into the syringe. The lower concentration found in the second ammunition can was due to poor sealing between the hose barb fitting and the ammunition can wall, which allowed air to be drawn in along with the gas sample. In the last ammunition can, the sample was pulled with the first hole unsealed, bringing in dilution air, hence the lower overall concentration for the last two ammunition cans sampled. Despite the concentration variability found inside all the ammunition cans, the concentrations determined were all much greater than the STEL, TLV-TWA of 0.3 ppm (0.4 mg/m<sup>3</sup>) and 1 ppm (1 mg/m<sup>3</sup>), respectively, recommended by the ACGIH.<sup>14</sup>

During the test, no PH<sub>3</sub> was detected in the chamber. The lowest detection limit was 0.05 ppm. To detect the PH<sub>3</sub> at this concentration inside the accelerated aging chamber, approximately 177 mg of PH<sub>3</sub> would have had to been off gassed into the chamber. Even if PH<sub>3</sub> did leak out into the chamber, it is unlikely that it would have been detected. Neither of the three ammunition cans (untouched or setup for sampling) showed any outward signs of bulging. The ammunition cans were not air tight (air sealed) and allowed the gas from within the ammunition can to leak out into the chamber. Future investigations should be performed to evaluate this observation and determine methods to possibly alleviate these elevated levels of PH<sub>3</sub>.

For the functionality test, all 16 grenades tested functioned properly even after being subjected to the long-term storage conditions discussed in Section 2.4.1. All grenade firings were recorded by video except for that of grenade #1.

#### 4.7 Aquatic Toxicity Testing

The extract produced from smoke aerosol had a resulting pH = 2.5 at 100% extract. The acute toxicity ( $\leq$ 24 hr) with the ceriodaphnia and *Vibrio fischeri* resulted from the shift in pH caused by adding extract to the test media. When the smoke aerosol extract was pH adjusted before its addition to test media, the acute toxicity was practically eliminated.

The extract produced from the smoke residue had a resulting pH = 6.8 at 100% extract. Exposures to the smoke residue extract caused minimal acute toxicity responses in either Ceriodaphnia or *Vibrio fischeri* at the concentrations tested.

The toxicity results from the smoke aerosol and residue extracts were scored (Table 23) using the Chemical Scoring System for Hazard and Exposure Identification.<sup>28</sup> This system is typically used in the preliminary screening process, and is not intended to be a substitute for Environmental Risk Assessments. The system assigns a score based on the acute and/or chronic toxicity data. When multiple species data are available, the final aquatic toxicity

scoring of the material of interest should be based on the most sensitive species and within the species, the most sensitive criteria (acute or chronic NOEC data) should be used. The scoring system developed by O'Bryan and Ross<sup>28</sup> scores toxicity using EC<sub>50</sub> and chronic NOEC values. This system is based on scoring from 0 to 9, with 9 being the most toxic. However, this system does not rank the scores using common terms typically used in mammalian toxicity rankings. The U.S. Fish and Wildlife Service (USFWS) published a Research Information Bulletin<sup>29</sup> suggesting relative aquatic toxicity terms based on EC<sub>50</sub> data. The ranking system considers EC<sub>50</sub> results >1000 mg/L to be "Relatively Harmless" and results <0.01 mg/L as "Super Toxic." Similar descriptive rankings are used by Kamrin.<sup>30</sup>

In this study, the *Vibrio fischeri* (microtox assay) was the most acutely sensitive species tested and received a score of 4 (slightly toxic) when exposed to smoke aerosol extract. This score may not be realistic and should be viewed with caution. The microtox media has no buffering capacity, and the pH shift after the addition of smoke aerosol extract is considerably greater than when the extract was added to the Ceriodaphnia media. For example, the pH of microtox media when smoke aerosol extract was added to produce a concentration of 12.9 mg/L was 4.3. The pH of Ceriodaphnia media when smoke aerosol extract was added to produce a concentration of 12.5 mg/L was 7.1.

The 7-day reproductive NOEC was the most sensitive end point for Ceriodaphnia when exposed to smoke aerosol extract. The 7-day reproductive NOEC was 12.5 mg/L, which received an aquatic toxicity score of 1, which was ranked as practically non-toxic (Table 23). The pH adjusted smoke aerosol and residue extracts for acute and chronic criteria received a score of 0 and were ranked as relatively harmless.

Table 23. Toxicity scores for Ceriodaphnia and microtox tests results. Scores are based on two criteria rating scales, acute  $\leq$ 96-hr exposures and chronic reproductive NOEC. The rating scale for chronic toxicity is one order of magnitude lower than the acute rating scale.

<i>Test Species</i>	<b>Toxicity Criteria</b>	<b>Score*</b>	<b>Ranking</b>
<i>Vibrio fischeri</i>			
Aerosol	5-min EC <sub>50</sub> = 15.4 mg/L	4	Slightly Toxic
	15-min EC <sub>50</sub> = 16.2 mg/L	4	Slightly Toxic
Aerosol (pH Adjusted)	5-min EC <sub>50</sub> > 3,313.3 mg/L	0	Relatively Harmless
	15-min EC <sub>50</sub> > 3,313.3 mg/L	0	Relatively Harmless
Residue	5-min EC <sub>50</sub> > 3,000 mg/L	0	Relatively Harmless
	15-min EC <sub>50</sub> > 3,000 mg/L	0	Relatively Harmless
<i>Ceriodaphnia dubia</i>			
Aerosol	24-hr EC <sub>50</sub> = 225 mg/L	1	Practically Non-Toxic
	7-day NOEC = 12.5 mg/L	1	Practically Non-Toxic
Aerosol (pH Adjusted)	24-hr EC <sub>50</sub> = 1,648 mg/L	0	Relatively Harmless
Residue	24-hr EC <sub>50</sub> = 2,616 mg/L	0	Relatively Harmless
	7-day NOEC = 125 mg/L	0	Relatively Harmless

\*Scoring criteria is based on a scale of 0 – 9, with 9 being the most toxic.

The most toxic extract was produced from the smoke aerosol. The aerosol was collected on a filter pad in an enclosed shed, which creates extremely high concentrations. In this study, we combined the aerosol material from three pads from different disseminations to yield a concentration of 3,313.3 mg/L. In an open-air deployment of the 66mm RP grenade, this concentration may not be realistic. Modeling or open-air down range smoke aerosol sampling should be conducted to determine if these concentrations would exist during deployment. Only then can the environmental impact from the 66mm RP grenade be realistically determined.

## 5. CONCLUSIONS

The creation and development of safe and effective smokes and obscurants is of great importance to the U.S. Military. One important point to emphasize is that there is no smoke formulation that is non-toxic. The role of development is to create the “safest” smoke formulation possible that would retain operational efficiency. The United States Marine Corps established the RP Grenade, 66mm Smoke Screening IR, Vehicle Launched MK1 MOD0 program to satisfy the need of redesigning the previously fielded M76 family of obscurants developed by the United States. Potential human health and environmental risks associated with the RP smoke grenade have been evaluated by making comparisons against limits established by regulatory agencies.

Data, when compared to other obscurants, suggest that the RP 66mm smoke grenade does not create additional risks upon dissemination. Combustion products, inorganic

anions, metal oxides, particle size, Volatile Organic Combustion Products (VOCs), and aquatic toxicology were all evaluated. Particle size analysis revealed, for this particular test, an MMAD, a  $\sigma_g$ , and a respirable mass percentage calculation for each 66mm RP grenade dissemination gave an average value of 3.743  $\mu\text{m}$ , 1.978, and 50.594%, respectively. However, dissemination of the smoke grenade would not be done inside an enclosed space; hence, these values are not relevant to describe the particle size of the smoke aerosol from a real world scenario. As such, the aerodynamic particle sizer was used to determine the particle size of the smoke aerosol down wind of an activated grenade. The particle size determined from the aerodynamic particle sizer gave an MMAD and  $\sigma_g$  of  $1.032 \pm 0.06$  and  $1.332 \pm 0.03$ , ( $n = 6$ ), respectively, with a respirable mass of 99.201%. This MMAD and  $\sigma_g$  indicate that the particle size would be  $\leq 1 \mu\text{m}$  in an open-air dissemination, which more closely resembles a real-world scenario. The VOC concentrations quantitated were not of any toxicological significance, with all concentrations less than the STEL [American Conference of Governmental Industrial Hygienists (ACGIH)]. As for the other VOC not quantitated, it would be expected that the concentrations would be similar to the quantitated values. However, without quantitation, this can only be considered speculative. Of the inorganic gases, carbon monoxide (CO), hydrogen cyanide (HCN), and formaldehyde (HCOH) exceeded their respective TLV-TWA and/or STEL limits as published by the ACGIH. Sulfur dioxide was only slightly higher than the respective STEL. Aerosol characterization of the metals also confirmed that the predominant portion of the aerosol (>55%) was comprised of phosphoric acid ( $\text{H}_3\text{PO}_4$ ), as expected for RP, with smaller percentages of potassium hydroxide (KOH), and magnesium oxide (MgO). All three concentrations (in milligrams per cubic meter) for each metal (MgO, KOH, and  $\text{H}_3\text{PO}_4$ ) significantly exceeded their respective regulatory limits as published by the ACGIH. The long-term storage did indicate that the current 66mm RP grenades may off gas phosphine ( $\text{PH}_3$ ) during storage, and the concentration most likely would exceed the recommended STEL for  $\text{PH}_3$  as indicated by the ACGIH. The aquatic toxicology studies, determined that first, the smoke aerosol extract was more toxic to the test organisms than the residue extract due to the acidic conditions created from the  $\text{H}_3\text{PO}_4$  produced during dissemination. When the smoke aerosol extract was pH adjusted before being added to the test media, the acute toxicity was reduced dramatically. If the smoke aerosol extract was not pH adjusted, the extract could be diluted to levels that eliminated pH affects. However, even when diluted, the smoke aerosol extract caused significant reproductive effects when compared to the control. The reproductive lowest observable effect considered for Ceriodaphnia was 12.5 mg/L, which received a toxicity score of 1 "Practically Non-Toxic". The smoke residue did not cause a detrimental shift in pH when added to the test media. The residue received a toxicity score of 0, ranking it as "Relatively Harmless" to *Ceriodaphnia dubia* and the microtox bacteria, *Vibrio fischeri*. The possible greatest concern for the current replacement 66mm grenade program was the high concentrations of  $\text{PH}_3$  found at the end of the long-term storage (accelerated aging) tests.

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